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Renewable and Sustainable Energy Reviews 13 (2009) 493–517
RENEWABLE & SUSTAINABLE ENERGY REVIEWS
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# Life cycle inventory analysis of the production of metals used in photovoltaics

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Received 4 September 2007; accepted 7 November 2007

## Abstract

Material flows and emissions in all the stages of production of zinc, copper, aluminum, cadmium, indium, germanium, gallium, selenium, tellurium, and molybdenum were investigated. These metals are used selectively in the manufacture of solar cells, and emission and energy factors in their production are used in the life cycle analysis (LCA) of photovoltaics. Significant changes have occurred in the production and associated emissions for these metals over the last 10 years, which are not described in the LCA databases. Furthermore, emission and energy factors for several of the by-products of the base metal production were lacking. This review article aims in updating the life cycle inventories associated with the production of the base metals (Zn, Cu), and defining the production paths and emission and energy allocations for the minor metals (Cd, Ge, In, Mo, Se, and Te) used in photovoltaics.
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*Keywords:* Photovoltaics; Life cycle analysis; Materials inventory analysis; CdTe; CIGS; Emissions; Metal production; Cadmium; Indium; Germanium; Selenium; Tellurium; Molybdenum; Gallium

## Contents



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1364-0321/$ – see front matter. Published by Elsevier Ltd.
doi:10.1016/j.rser.2007.11.012

## 1. Introduction

There is a need for up-to-date estimates on the emissions during the production of the constituents of photovoltaic (PV) modules, because such data are used to derive important conclusions regarding the environmental impacts of PV technologies. Significant changes have occurred in the emission factors associated with producing the metals used for semiconductors, coatings, and frames in PV modules. Emissions from smelters were greatly reduced over the last 10 years as companies strove to improve their environmental records. However, the databases used for life cycle analysis (LCA) models often are outdated. A cursory review of the major LCA databases, EcoInvent [1], ETH [2], DEAM [3], and IVAM4 [4], revealed some emission factors based on outdated information from 1980, with most sources dating before the mid 1990s. In addition, the "minor" metals (Cd, Se, Te, In, Ga, and Ge) that are by-products of base metal smelting (e.g., Cu, Zn, Pb, and Al), either are not included or are inadequately described. Among them, only cadmium is included in DEAM, only Se and Mo are included in EcoInvent, and IVAM4 has none. The emission factors for Cd in DEAM are the same with those for Zn although there are clear rules (e.g., ISO 14001) for avoiding allocation in the co-production of metals by dividing the process into distinct sub-processes.

This paper describes materials' environmental inventory analyses, which are the first step in the life cycle analyses of solar cells. CIGS solar cells, use Zn, Cu, In, Ga, Se, Cd, and Mo. CdTe cells use Cd, Cu and Te. Some amorphous Si solar cells use $GeH_4$. From these metals, Cu and Zn are primary (base) metals, which are extracted in large quantities for their value, whereas In, Ga, Se, Cd, Mo, Ge, and Te are minor metals generated as by-products of the production of the base metals.

In, Cd, Ge, and to small degree Ga are by-products of zinc production; most Ga is produced as a by-product of aluminum production. Some Cd is also produced in lead production. Se and Te are by-products of copper production.

Emissions from the non-ferrous metal industry were reported as the largest contributor to global emissions of As, Cd, Cr, Cu, In, Mn, and Zn in 1983 [5]. These emissions were debated by others [6]. Pacyna and Pacyna have compiled emissions from several regions of the world, based on both estimates and actual measurements (i.e., emission inventories); the most recent paper by these authors shows 1995 emission factors in comparison to those in 1983 [7]. According to these investigators emissions of trace metals have in average decreased from 1983 to 1995 by a factor of 2–3, mostly because of better emission controls in major smelters in Europe and North America. Comprehensive emission factors more recent than 1995 are not reported in the literature. Also, emission factors for the production of the minor metals are not reported.

Our study reviews the most current (post-2000) emission and energy data and examines the trends in the production of each of the four base metals and by-products. Emission factors for the four primary metal categories are reviewed and updated based on plant-specific information for plants in the US and Canada. Also European and global trends are discussed.

## 2. Methodology

The life cycle inventory (LCI) analysis involves data collection and calculations to quantify material and energy inputs and emissions outputs of a product system [8]. We specifically investigate the LCI of mining, smelting, and refining stages for Cu, Zn and their co-products based on process-based system boundaries. The inventory computation of co-products proceeds with established allocation rules, which were standardized in documentation.

The international standard organization (ISO) specifies a procedure (ISO 14041) for deciding such allocation [9]. It entails the following steps: (1) Allocation should be avoided, whenever possible, by dividing the process into sub-processes, and including the additional functions related to co-products. (2) Where allocation cannot be avoided, the system's inputs and outputs should be partitioned to reflect the underlying physical relationships between them (i.e., they must mirror the way the inputs and outputs are altered by quantitative changes in the

products or functions). (3) Where physical relationships alone cannot be established or used as a basis for allocation, inputs should be allocated between the products in proportion to the products' economic values.

According to the first rule of the ISO 14041, the emissions from the mining of the zinc ores to the recovery of saleable zinc are allocated to zinc and the emissions during the purification of the waste stream to extract a by-product, are assigned to the by-product.

For Cd, the case for avoiding co-allocation of energy and emissions between Zn and Cd is clear because Cd is an unavoidable by-product of Zn production. A few European smelters are stabilizing and storing this material in managed repositories, but most Zn smelters produce Cd metal as an unavoidable by-product since it is present in the zinc concentrate feed to the smelter. The production of zinc alone determines the amount of cadmium produced; demand for it has zero effect on the quantity of cadmium generated. The production of cadmium metal from the Cd/Cu cement is clearly a distinct process. Also purification of Cd, for example by distillation, should result in energy and emissions, which are totally attributed to Cd. Thus, the zinc cycle starts with mining the Zn ores and ends with generating the saleable Zn product, whereas the cadmium cycle starts with the Cd/Cu cement, and includes the steps related to the separation and purification of cadmium. This avoidance of allocation is in agreement with well-accepted LCA practices [10].

However, avoiding allocation was not attempted in this review as the data were reported in aggregated forms in our data sources, insufficient to disintegrate the production stages into sub-processes of purifying co-products. We allocated emissions and energy use based on mass output according to the second step of the ISO guidelines, and also based on the economic value of the produced metals in accordance to the third step of the guidelines.

## 3. Production of Zn and co-products (In, Cd, Ge, and Ga)

### 3.1. Mining and beneficiation

Zinc is found in the earth's crust primarily as sphalerite, a mineral containing zinc sulfide (ZnS). Sphalerite ores contain 3–11% zinc, along with 0.0001–0.2% cadmium (median concentration = 220 μg/g), <0.0001–0.01% indium, copper, lead, silver and iron, and small amounts of gold, germanium and thallium. Indium also exists in the ores of other base metals (e.g., copper, lead, and tin), but most of these deposits are too dilute for indium recovery. Also some deposits of tin and tungsten carry relatively high concentrations of indium, but indium from this type of deposits is difficult to process economically.

The major phases of mining include extraction (underground and open pit) and ore beneficiation (i.e., concentration). In underground mines, the ore is excavated by drilling machines, processed through a primary crusher, and then conveyed to the surface. In open-pit mines, the ore is loosened and pulverized by explosives placed in drilled holes and is scooped up by mechanical equipment. The ores are then transported to a concentration mill, which is usually at the metallurgical part of the operation. Mining generates large volumes of solid waste since the mining operation necessarily involves the removal of waste rock (gangue) in addition to the ore. Zinc ores are mined almost exclusively in underground operations.

The concentration of the metals in the recovered ore is done by crushing, grinding, screen separation, and flotation processes. Crushers, screens, and rod- and ball-mills reduce the ore to powder of 20–200 μm sizes. The particles are separated from the gangue and concentrated in a liquid medium by gravitation or by selective flotation, followed by cleaning, thickening, and filtering [11]. The most common separation method is froth flotation in which the crushed ore is mixed with water, treated with suitable reagents and then frothed by blowing bubbles into the mixture. The metal concentrates are dewatered, dried, and shipped to smelter processing [12]. The zinc concentrates are transferred to smelters/refiners to produce the primary metals (Fig. 1).

### 3.2. Zinc production

Zinc can be refined by either pyrometallurgical or hydrometallurgical treatment of its concentrates (Fig. 2) [13]. Older roast/retort smelters are no longer employed in North America and northern Europe. As of 2001, about 90% of the world's zinc production is done by the electrolytic process and about 8% by the pyrometallurgical imperial smelting process [14]. The trend towards electrolytic recovery continues and the last imperial smelter in England closed in 2003. The global demand for zinc is increasing and this growth is fueled by China, also the biggest producer, where the consumption of zinc increased by 10% in 2004.

There are four primary zinc-smelting operations in the United States. Three of them utilize electrolytic technology, and one uses an electrothermal process [12]. In Canada, there are four zinc producers, all of which use electrolytic processes for zinc refining. Canada is the second largest zinc producer in

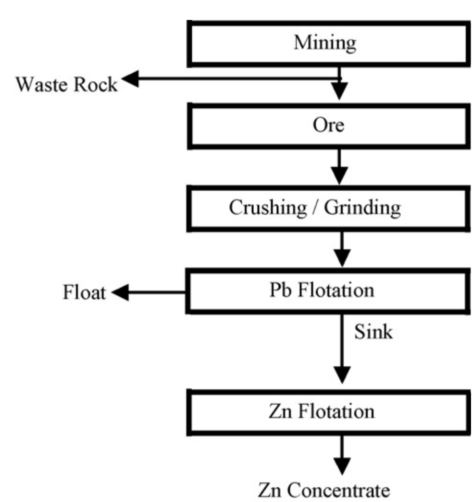


Fig. 1. Flow of zinc mining and beneficiation.

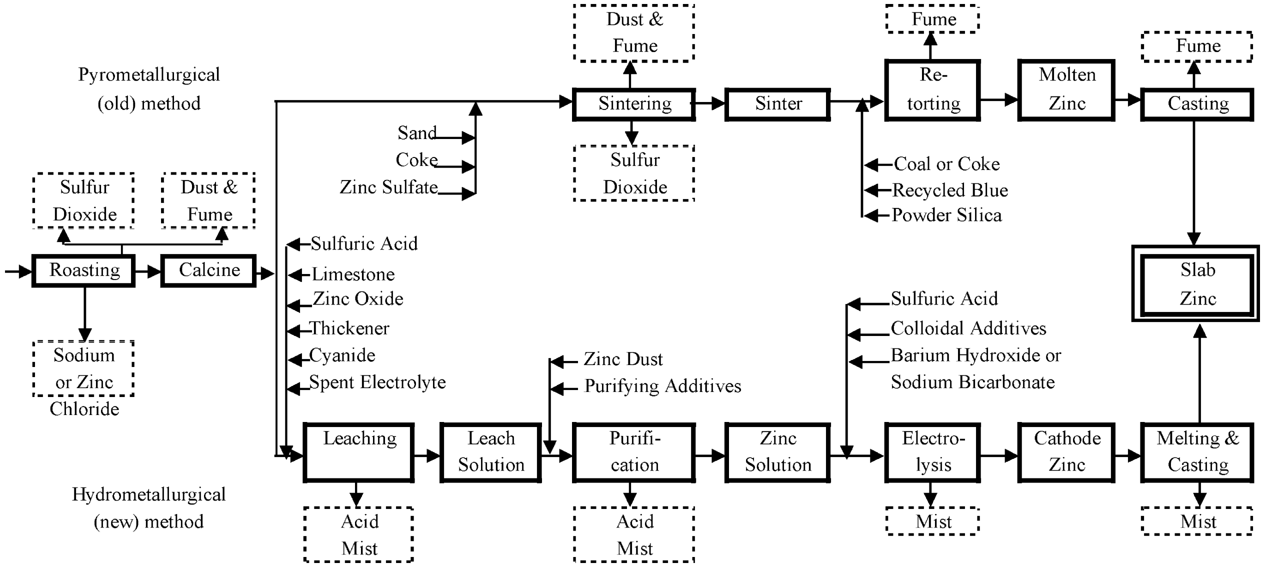



Fig. 2. Generalized process flow for primary zinc smelting [13].

the world, after China. The total Canadian refined zinc production in 2002 was 793,000 tonnes and that of the US was 289,000 tonnes. The zinc ore production from mines in the two countries was 916,000 and 783,000 tonnes of crude metal correspondingly. The US exports most of its mine production for processing in other countries. In addition to Zn, the zinc smelters in North America also produce 100% of the Cd, Ge, In, and Th, 10% of Ga, 6% of Pb, 4% of Ag and 3% of Au used in the region [15]. All the zinc smelters in North America also produce cadmium as an unavoidable by-product; before cadmium production started in the US in 1907, about 85% of the Cd content of the zinc concentrates was emitted to the environment during roasting and fractional distillation of zinc metal [16]. Indium and germanium are only produced in two Canadian facilities, the Teck Cominco, Trail and the Falconbridge, Kidd Creek facilities. The electrolytic zinc process consists of five main operations: roasting, leaching, purification, electro-deposition, and melting/casting (Fig. 3). In some operations roasting and the first part of leaching are replaced by pressure leaching:

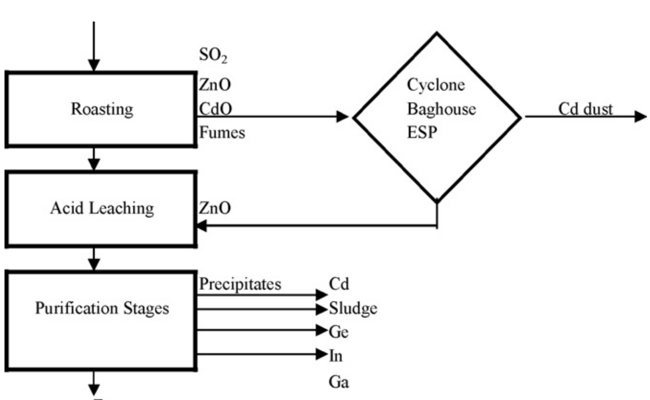



Fig. 3. Flows of zinc refining and by-product production [13].

(i) In roasting, the sulfide concentrates are fed to fluidized-bed furnaces where they are burnt with air and direct oxygen. Approximately one-half of the oxidized concentrate (zinc calcine) leaves the roasters in a melted phase by overflow and the rest is carried by the roaster gases. Zinc calcine, is mainly zinc oxide with small amounts of iron, cadmium, and other metals. Calcine is cooled, passed through a mill and collected in cyclones and electrostatic precipitators. The roaster gases, containing about 8% sulfur dioxide, are cooled in a waste-heat boiler, to recover heat and generate steam. They are usually treated to recover mercury, before they are fed into a sulfuric acid plant. In alternative pressure leaching operations, the zinc concentrates are treated with acid and oxygen in vessels under 150 °C and 1400 kPa. Elemental sulfur is extracted in series of flotation cells and the slurry of zinc sulfate is pumped into the leaching plant for further processing.

(ii) Leaching of the metals from the calcine is accomplished by sulfuric acid, which is typically produced from $SO_2$ in house. This process dissolves the zinc to make a solution of zinc sulfate and other acid-soluble metals. Iron is precipitated and filtered from the process as a residue. Depending on the ore, the residue may also contain lead, copper, silver, and gold. Cadmium is not removed in the iron purification step, and must be removed by cementation with Zn metal powder to produce a Cd/Cu cement. The leachate is sent to the purification section.

(iii) In purification, cadmium, germanium, indium, and gallium as well as iron, copper, cobalt and nickel are removed, usually in three stages. These are described in Sections 3.3–3.6 below.

(iv) Zinc is recovered from the sulfate solution by electro-deposition on aluminum sheet cathodes. The Zn-covered cathodes are removed periodically and the pure zinc layer covering them is stripped off and fed into induction furnaces. Also sulfuric acid is regenerated in this stage.

(v) The final steps in zinc production are melting, casting, and alloying. The zinc stripped off from the cathodes is melted, and cast into ingots, slabs, or larger blocks of slab ready for delivery to customers [14,17].

The imperial smelting process uses sintering and smelting instead of roasting and electrolytic recovery. The sintering process generates much higher air emissions than roasting.

### 3.3. Cadmium production

The feed material for producing cadmium consists mainly of residues from the electrolytic production of zinc, and of fume and dust collected in baghouses from emissions during pyrometallurgical processing of zinc and lead smelting. The cadmium sponge, a purification product from precipitating zinc sulfate solution with zinc dust at the zinc smelter, is 99.5% pure cadmium. This sponge is transferred to a cadmium recovery facility and is oxidized in steam for 2 days or so. The product, cadmium oxide, along with particulates collected in baghouses, is leached with spent cadmium electrolyte and sulfuric acid to produce a new recharged electrolyte. Impurities are precipitated with a strong oxidizing agent. The wastes are refined for other uses or stockpiled, until a use can be found for them. Non-corrosive anodes are used during electrowinning. Additives (often animal glue) are used to enhance the smoothness of the resulting cadmium cathode. The cathodes are removed about every 24 h and are rinsed and stripped. The stripped cadmium is melted under flux or resin and cast into shapes.

About 10% of cadmium is produced from the fumes and dusts of lead smelters. These are concentrated to 8–60 wt% cadmium and shipped to the cadmium recovery plant where they are reacted with sulfuric acid. The resulting calcined cadmium sulfate and impurities are roasted and then leached with water to dissolve the cadmium. The cadmium sulfate solution is first filtered to remove the lead sulfate, which is recycled to the lead smelter and then further purified by electrolytic separation. The resulting electrolyte is 99.995% pure. The cadmium is melted and cast into shapes. The spent electrolyte is recycled at the cadmium recovery plant.

In a slightly different route, purification residues from the oxide and the sulfide-leaching processes are further leached with sulfuric acid and filtered through three stages to remove zinc, copper, and thallium before recovering the dissolved cadmium. Cadmium can be further purified with vacuum distillation to 99.9999% purity [17].

The total loss in emissions and residues at cadmium plants is about 5% [16]. Thus, about 95% of Cd from Cd concentrates is converted in metallurgical grade (99.99%) metal, which is used in all current applications, except for semiconductor CdTe and CdHgTe. High-purity (i.e., 99.999–99.9999%) Cd powder is produced by electrolytic purification and subsequent melting and atomization or by vacuum distillation followed by zone refining.

### 3.4. Indium production

Indium is recovered as a by-product of zinc production from the fumes, dusts, slags, and residues in zinc smelting [18]. The total global production in 2003 was about 300 metric tonnes [19].

The information on In and Ge production is sketchy since a technology to recover them is proprietary, and large part of the production is from China. Below we list a description of such recovery from Ullmann's encyclopedia [20] and some general information from manufacturers' reports.

Following the zinc operations described in Section 3.2, after roasting, the zinc oxides undergo leaching and purification, which produces indium. Zinc oxide is first leached with dilute sulfuric acid to remove zinc, and the residue is leached again with dilute hydrochloric acid [20]. This leaching removes most of the lead and also, a small portion of indium and arsenic from the residues. The residue contains about 20% arsenic, 5–10% tin, 5% antimony, and 0.2% indium. In the next step, soda is added to the remaining filtrate to precipitate the majority of indium. This is the major stream in indium extraction. The concentration of metals in the filtrate are about 10–50 mg/L of indium, 40 g/L of zinc, 6 g/L of cadmium, and 1 g/L of arsenic. About 10% of the indium remains in the residue, which is leached with sodium hydroxide to create crude indium hydroxide, containing 20% indium, 6% zinc, 1.5–3% arsenic, and 0.5–2% cadmium [20]. The crude indium hydroxide is leached with dilute hydrochloric acid. The indium solution is purified by cementation of copper and arsenic with iron, followed by cementation of tin and lead with indium [20]. Finally, to remove the indium, aluminum is added to create indium cement. This sequence is shown in Fig. 4.

Teck Cominco Ltd. is one of the world's largest indium producers, generating approximately 36 tonnes of high-purity (99.998% and 99.9999%) indium per year. It recovers indium from gaseous streams at its integrated zinc and lead in Trail, British Columbia, Canada. Fumes and other particulates from the lead smelter are transferred to the zinc facilities for hydrometallurgical separation and from there to the high-purity indium plant. Fumes generally contain only 0.05–0.2% In or Ge. The plants then leach the fumes to extract In and Ge into solution (along with Zn and Cd) to separate them from the lead sulfate residue. After a first leaching, slurry is settled to remove a lead oxide residue which is pumped back into the lead smelter, and the clear solution is passed on to a second leach. There, the slurry is partially neutralized with direct fume addition and ferric iron to precipitate germanium, indium, arsenic and antimony. This precipitate is the feed for the indium/germanium recovery plant. The residues from the oxide leaching plant second leach are re-leached with sulfuric acid to dissolve the contained germanium and indium. After filtration, the clear solution is processed in a solvent extraction (SX) unit where both metals are recovered and subsequently re-precipitated to a product for further purification.

The Falconbridge Limited's Kidd Creek operation in Timmins, Ontario is another major producer of indium. The general flowsheet of indium recovery from zinc processing at

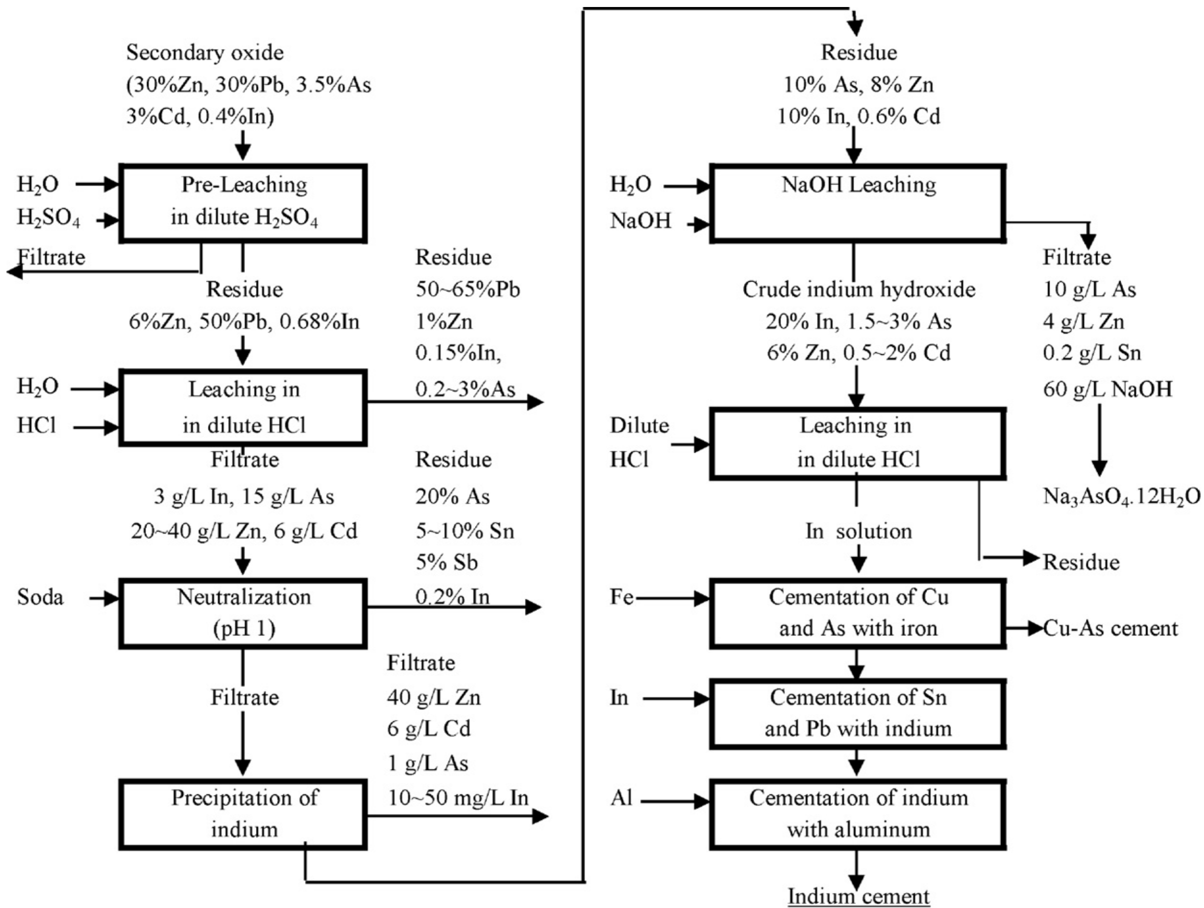



Fig. 4. Recovery of indium from secondary zinc oxide [20].

Kidd Creek is shown in Fig. 5. Similar to Teck Cominco's process indium is extracted from the leachate by the solvent extraction (SX) method. The Kidd Creek's indium product is then shipped to the United States for further refining.

Indium Corporation of America, Utica, NY, and Arconium Specialty Alloys, Providence, RI produce indium metal and indium products by upgrading imported indium metal. Lower grade (99.97%) and standard grade (99.99%) imported indium is refined to purities of up to 99.9999% in these facilities.

### 3.5. Germanium production

The major source of germanium is the mineral ore germanite ($Cu_3(Ge,Fe)S_4$), which is associated with zinc ores and fly ash of certain coals. It is also a constituent of argyrodite ($Ag_8GeS_6Al$), a more rare mineral. World refinery production was reported to be about 70 tonnes in 2001 and about 50 tonnes in 2002. Zinc recovery represents the largest single source of germanium, with some additional material extracted from electrolytic refining operations for copper and lead [22–24]. From the four Canadian producers of zinc only Teck Cominco is reported to produce germanium. The production of germanium consists of generation of germanium concentrate followed by actual production of germanium and germanium oxide. Germanium tetrachloride is hydrolyzed to the dioxide state then reduced to pure metal by carbon or hydrogen. Fractional distillations of the tetrachloride separates germanium from other metals and zone refining produces very high purity (up to nine mines) of germanium for semiconductor use.

Some facilities in the former Soviet Union probably recover germanium from the fly ash of power plants [24]. In Canada, Argento Plata Metals recovers germanium from electronic scrap along with gallium and indium, using a hydrometallurgical process

### 3.6. Gallium production

Gallium occurs in very small concentrations in many rocks and ores of other metals. It is a scarce element found most commonly in association with aluminum, germanium and zinc. About 5% of the global production of gallium is obtained from residues in zinc processing; 95% of the global supply is obtained as a by-product of alumina production from bauxite. In Zn facilities, as discussed earlier, the zinc ore is leached with sulfuric acid, and the removed impurities include gallium, aluminum and iron. After the zinc is removed, the solution is neutralized to precipitate the metal hydroxides [25]. Hydrochloric acid is used to dissolve gallium and aluminum from the metal hydroxides. Then the gallium is separated from aluminum by solvent extraction with ether. From the distillation, a highly concentrated

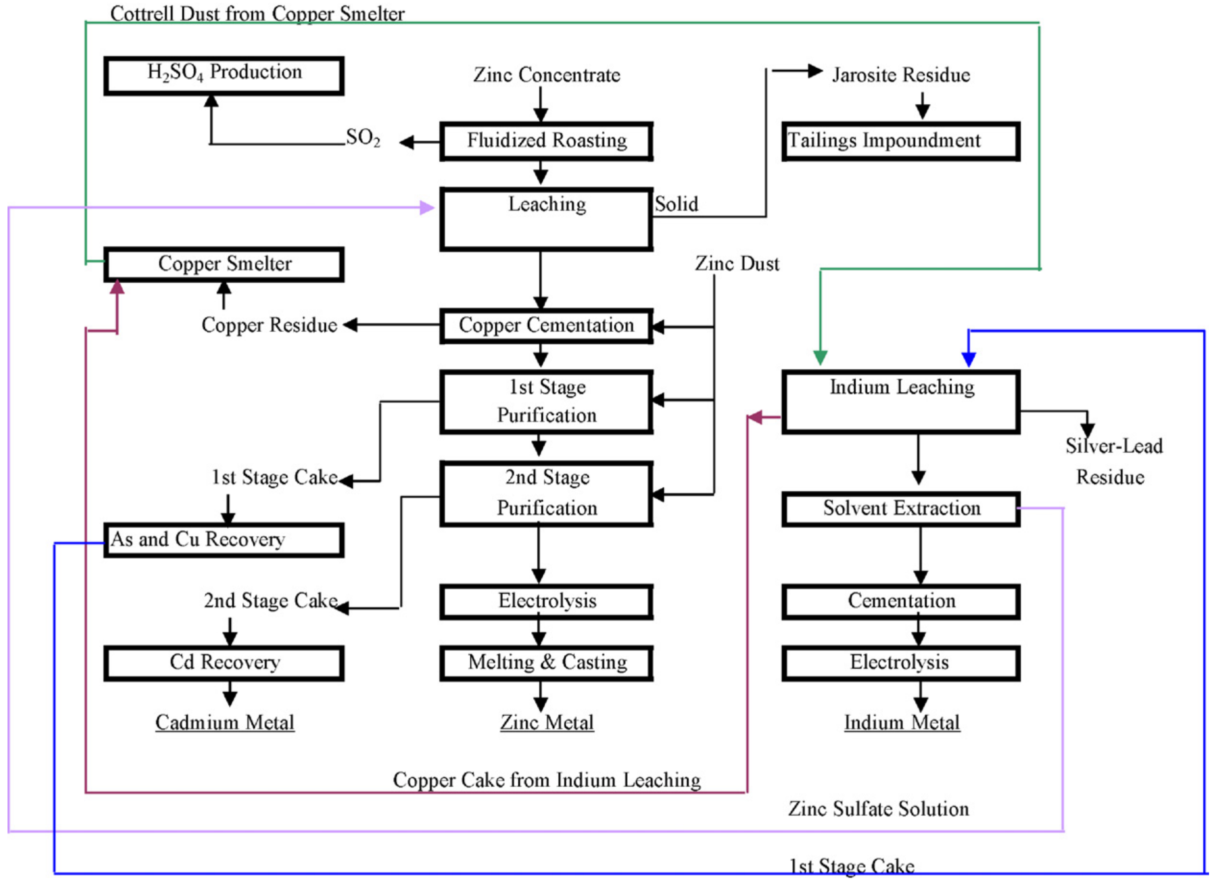



Fig. 5. The recovery of indium and cadmium from zinc processing at Kidd Creek, Canada [21].

gallium residue is produced, which still contain iron. Gallium is removed in liquid form by a caustic solution leaving the iron as solid. Finally, the crude gallium is recovered by electrolysis. In Zn smelters, when Ga is not recovered, it ends in the slag.

### *3.7. Purification of cadmium, indium and germanium for solar cell applications*

Teck Cominco reports that all the cadmium they produce is ultra-pure grade (i.e., 99.9999%). Purification residues from their leaching plants undergo additional leaching with sulfuric acid and are filtered through three stages to remove zinc, copper, and thallium. The final step is vacuum distillation [17].

High-purity Cd and Te powders from other manufacturers are produced by electrolytic purification and subsequent melting and atomization (see Fig. 6), and by vacuum distillation. Both methods are proprietary and information about emissions is not published. According to industry sources, electrolytic purification does not produce any emissions and all waste is recycled. The melting and atomization steps needed to form the powder produce about 2% emissions that are captured by HEPA filters [26]. The efficiency of HEPA filters in collecting particulates of mean diameter of 0.3 μm is 99.97%.

Zone refining involves four steps during which the concentrations of impurities are quickly reduced below levels detected by standard analytical techniques [27–30].

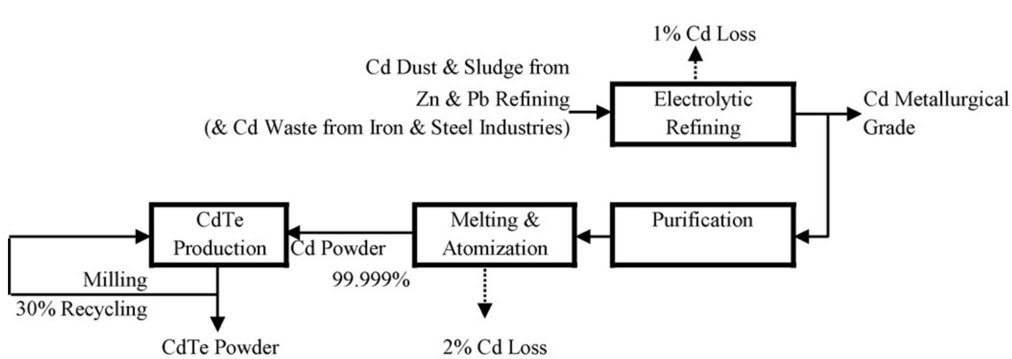



Fig. 6. Cd Flows from Cd concentrates to CdTe [13].

Table 1
Particulate emission factors in zinc smelting by thermal (old) and electrolytic (new) methods [11]

| Process | Uncontrolled emissions (kg/tonne of zinc ore) | Post-control emissions (kg/tonne of zinc concentrate) | Estimated Cd emissions[a] (kg/tonne of zinc concentrate) |
|---|---|---|---|
| Roasting | | | |
| Multiple hearth | 113 | ND | ND |
| Suspension | 1000 | 4 | 0.02 |
| Fluidized bed | 1083 | ND | ND |
| Sinter plant | | | |
| Uncontrolled | 62.5 | NA | NA |
| With cyclone[b] | NA | 24.1 | 0.14 |
| With cyclone and ESP[b] | NA | 8.25 | 0.05 |
| Vertical retort | 7.15 | ND | ND |
| Electric retort (electrothermic process) | 10.0 | ND | ND |
| Electrolytic process | 3.3 | ND | ND |

[a] Cadmium content in particulates is estimated assuming a zinc/cadmium ratio of 200 (0.5% Cd); ND: not detected.
[b] Data not necessarily compatible with uncontrolled emissions.

### *3.8. Emission factors in the co-production of Zn, Cd, In, Ge, and Ga*

#### *3.8.1. Mining*

The extraction, crushing, ore beneficiation, transpot and wind-borne losses could generate significant levels of dust. A range of 0.003–27 kg dust/tonne of ore is reported in the Word Bank Pollution Prevention and Abatement Handbook for global operations during the 1980s and the first half of the 1990s [31], but this range inlcudes surface mining that generates much higher emissions. All North American production of zinc is from undrground mines. In addition, the major metal producers in the continent have greatly improved their operations over the last 10 years and they implement controls which minimize dust emissions. Water sprays are used to control generation, and scrubbers and cyclones are utilized to collect the dust. Teck Cominco uses a wet grinding proces resulting in a slurry from which, reportedly, there are no dust emisions [32]. Falconbridge Ltd. reports no air emissions for their Kidd mining division, althought they report metals released to water. Therefore, the low limit of the total particulate range (i.e., 0.003 kg/tonne ore) was assumed herein to represent the most likely conditions in today's mining operations in North America.

#### *3.8.2. Metallurgical operations*

Production of zinc from zinc concentrates produces air emissions, process wastes, and solid-phase wastes. The zinc roasting process primarily emits sulfur dioxide. These emissions often are recovered on-site in sulfuric acid production plants. Zinc roasters also generate particulates containing cadmium, lead and other metals. The particulate emission streams are controlled with cyclones and electrostatic precipitators (ESPs), and the particulates collected in the control equipment constitute hazardous waste. As discussed later, this waste comprises a part of the feed to the cadmium-production plant. Table 1 shows the US EPA's estimates of particulate emissions for US plants. We estimated their cadmium content based on a typical concentration of Cd in Zn concentrate (e.g., 0.5%).

Wastewater produced from leaching, purification and electrowinning usually is treated and reused, or discharged. Solid wastes include slurries from the sulfuric acid plant, sludge from the electrolytic cells and copper cakes, and the by-products of zinc production from the purification cells which contain cadmium, germanium, indium, and other metals. Much of the waste is RCRA [33] hazardous waste. Copper cakes are captured and sold to copper processing plants. Purification by-products and other solid wastes are recycled or stockpiled until they can be economically used.

Berdowski et al. [34] reported on the emissions from zinc-smelting operations in other countries; these are summarized in Table 2. Cd emissions vary widely depending on the ore used and the abatement measures applied. For electrolytic production, emission factors of 0.5 g Cd/tonne Zn were reported in

Table 2
Emission factors for primary zinc production (g/tonne product) [34]

| Compound | Germany 1991 | | Poland 1980–1992 | | The Netherlands 1992 | Europe 2002 | |
|---|---|---|---|---|---|---|---|
| | Thermal | Electrolytic | Thermal | Electrolytic | Electrolytic | Thermal | Electrolytic |
| Cadmium | 100 | 2 | 13 | 0.4–29 | 0.5 | 50[a] | 0.2 |
| Lead | 450 | 1 | 31–1000[b] | 2.3–467 | – | 1900 | – |
| Mercury | 5–50 | – | – | – | – | 8 | – |
| Zinc | – | – | 420–3800 | 47–1320 | 120 | 16,000 | 6 |

[a] With vertical retort and limited abatement: 200 g/tonne product; with imperial smelting furnace: 50 g/tonne product.
[b] Limited abatement.

Table 3
Production and emissions at the Trail Smelter and Refineries, British Columbia, Canada [17]

| | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 |
|---|---|---|---|---|---|---|---|
| Annual production (tonne) | | | | | | | |
| Zinc | 274,300 | 288,700 | 272,900 | 168,100 | 269,000 | 283,100 | 296,000 |
| Lead | 63,900 | 75,700 | 91,300 | 55,200 | 80,700 | 87,800 | 84,300 |
| Cadmium | 969[a] | 1020[a] | 964[a] | 594[a] | 950[a] | 1000 | 1050[a] |
| Specialty metals | N/A | 28 | 28 | 28 | 28 | N/A | N/A |
| Indium | 31[a] | 33[a] | 31[a] | 19[a] | 31 | 34 | 42 |
| Silver | 463 | 431 | 463 | 348 | 550 | 569 | 613 |
| Gold | 3 | 2 | 2 | 2 | 5 | N/A | N/A |
| Fertilizer | 273,000 | 240,700 | 220,300 | 167,500 | 225,000 | N/A | N/A |
| Cd release to air (g Cd/tonne metal) | N/A | 1.64 | 0.69 | 0.45 | 0.27 | N/A | N/A |
| Cd release to water (g Cd/tonne metal) | N/A | 0.57 | 0.79 | 0.76 | 0.59 | N/A | N/A |

[a] Estimated based on 2003's production levels.

1992 for the Netherlands, 2 g Cd/tonne Zn in 1991 for Germany, and a range of 0.4–20 was reported for 1980–1992 for Poland. More recent (2000) data show 0.2 g Cd/tonne of metal product for North European countries [35,36].

Slightly higher emissions (i.e., 0.27 g Cd/tonne metal) are reported from the Teck Cominco integrated zinc- and lead-smelting and refining facilities in Trail, British Columbia, Canada [37]. Most likely, the difference is due to the pyrometallurgical lead production in this facility. In addition to zinc and lead, 18 other products are formed including silver, gold, indium, germanium, bismuth, copper products; and sulfur compounds (e.g., ammonium sulfate fertilizer, sulfuric acid, liquid sulfur dioxide, and elemental sulfur). The reported cadmium releases from all operations at Trail in 2002 were 95 kg in air and 208 kg in water; they correspond, per tonne of metals produced, to 0.27 g of Cd air emissions, and 0.59 g of water discharges (Table 3). Only total emissions from all operations were reported; the contribution of the cadmium plant to these emissions is difficult to determine because feeds and residuals were transferred between plants in the same facility. Also, the Trail smelting facility processes metal scrap and other waste in addition to Zn and Pb ores. These data show a continuing improvement from 1989 to 2002. The actual emissions of Cd into the air declined by 84% between 1999 and 2002 (Table 3). Releases in the water within this period remained approximately the same. The production and emission factors from another very large Canadian facility, the Falconbridge Limited's Kidd Creek Smelter and Refineries, are listed in Table 4. The reported cadmium releases from all operations at Kidd Creek in 2001 was 1.87 g/tonne metal air emissions, and 0.38 g/tonne metal of water discharges.

### *3.9. Energy factors in the co-production of Zn, Cd, In, Ge, and Ga*

#### *3.9.1. Mining*

At Teck Cominco's Reg Dog mine, which supplies 51% of the feedstock of the Trail metallurgical operations, the fuel (primary) energy consumption in the period of 1995–2003 was about constant at 0.8 GJ/tonne of ore mined. The zinc concentration in the ore is about 21%, which corresponds to 3.8 GJ/tonne metal produced [17]. In the Falconbridge Kidd Creek mining operation, energy use of 0.02–0.03 MWh/tonne of ore mined is reported for the period of 1997–2000; whereas 0.19 MWh/tonne is reported for 1996 and 0.15 MWh/tonne for 2001. The ore mined in this location contains about 5% zinc and 2.1% copper. Correspondingly the fuel energy factors are 1.4–13.7 GJ/tonne zinc and 3.4–32.6 GJ/tonne copper [37].

Table 4
Production and emissions at Falconbridge Ltd. Kidd Creek Smelter and Refineries, Timmins, Ontario

| | Year | | | | |
|---|---|---|---|---|---|
| | 1997 | 1998 | 1999 | 2000 | 2001 |
| Annual production (tonne) | | | | | |
| Copper | 122,953 | 124,147 | 122,966 | 124,529 | 132,100 |
| Zinc | 126,320 | 145,100 | 131,100 | 141,400 | 140,073 |
| Cadmium | 820 | 940[a] | 850[a] | 920[a] | 910[a] |
| Indium | 24 | 22 | 20[a] | 21[a] | 21[a] |
| Sulfuric acid | N/A | 543,700 | 496,400 | 545,800 | 514,300 |
| $SO_2$ emissions (kg/tonne metal) | 20.95 | 18.31 | 20.25 | 14.44 | 14.29 |
| $CO_2$ emissions (kg/tonne metal) | 1373 | 1210 | 1196 | 1213 | 1200 |
| Cd release to air (g Cd/tonne metal) | 2.44 | 2.15 | 1.91 | 2.07 | 1.87 |
| Cd release to water (g Cd/tonne metal) | 0.56 | 0.19 | 0.48 | 0.78 | 0.38 |

*Data sources*: 2001 Action Plan and Performance Data, Site Reports of Kidd Metallurgical Division, Falconbridge Limited, http://www.falconbridge.com; Falconbridge Ltd., Energy Intensity Improvement and Green House Gas Reduction Action Plan, 2000, Pollution Probe, sulfur dioxide and toxic metal emissions form smelters in Ontario, February 2003, http://www.pollutionprobe.org/Publications/Smelter%20Report.pdf.

[a] Estimated based on 1997's production level.

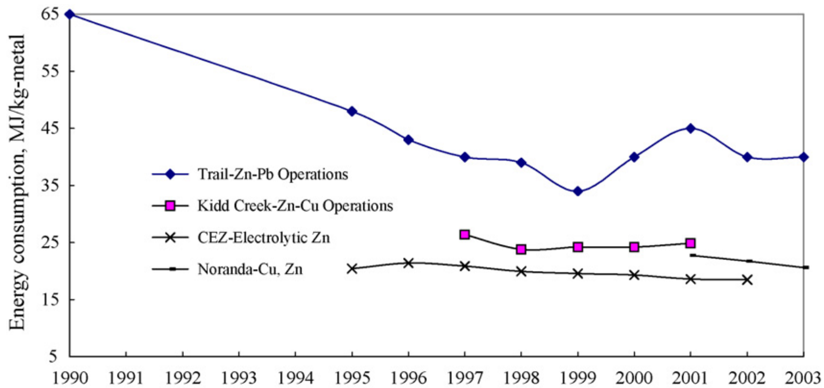



Fig. 7. Energy intensity in major Canadian Zn–Pb and Zn–Cu operations.

*3.9.2. Metallurgical operations*

At Teck Cominco's Trail operations, the total energy consumption in 2003 was 40 GJ/tonne metal, down from 65 GJ/tonne metal in 1990 [37]. These data include the entire site and all processes that use energy. Teck Cominco runs several additional unit operations, compared with most other smelters, to produce a much wider range of products and all of these unit processes consumed energy. For example, most zinc plants simply put their residues into a tailing pond while Teck Cominco smelts them and use a slag fumer to recover zinc and concentrate elements like In and Ge. They also run a precious metals refinery and lead refining unit that consume disproportionally high energy. In addition they produce ammonium fertilizer, liquid $SO_2$ and gypsum, all of which consume energy that is allocated to the metal production. The electric power for the Trail operations is generated by the company's Waneta hydroelectric dam. Lead concentrates are received in gondola cars from the Sullivan mine in Kimberley, B.C. and from various other custom concentrators in the US and South America.

In the Falconbridge Kidd Creek metallurgical operations, the total energy consumption is reported to be about 25 MJ/kg metal in the period 1997–2001. The metallurgical division consists of a concentrator, a copper smelter and refinery, a zinc plant, a cadmium plant, an indium plant and a sulfuric acid plant. The Kidd Creek's ore contains 2.10% copper and 5.0% zinc. Both facilities use electrolytic production of zinc and pyrometallurgical production of lead (Kivcet ''flash'' smelter, Trail) or copper (Mitsubishi ''bath'' smelter, Kidd Creek). The total energy intensities of the four facilities are shown in Fig. 7.

A recent life cycle analysis of lead and zinc production in Australia [14] shows that when zinc and lead are produced separately, zinc by the electrolytic process and lead by the blast furnace process, the zinc production is more than two times more energy intensive as lead production (i.e., 48 MJ/kg versus 20 MJ/kg). The production of zinc via imperial smelting process is reported to be 36 MJ/kg Zn [14].

*3.9.3. Inventories of emissions and energy for zinc and co-products*

Inventories of emissions and energy for zinc and co-products based on the data discussed in Section 3.9 are presented in Table 5. The life cycle inventories can be readily used by the LCA practitioners and constitute the most up-to-date energy and emissions data available in the production stage. For the energy usage in the mining stage, we use the 1997 data of Annual Survey of Manufacturers (ASM) [38], which contains the most recent US data for the amount of electricity and fuel consumed along with ore mined. For the energy usage during the smelting and refining, the value of Canadian electrolytic zinc (CEZ) is used as it best represents the energy associated with the zinc process only. Data of emissions to air and water during the smelting stage are from the report of Kidd Creek [21].

*3.10. Production of lead and by-products (Cd)*

Similarly to zinc ores, lead-bearing ores are processed by crushing, screening and milling to reduce the ore to powder, they are concentrated by flotation, separation and drying and the concentrates are transferred to smelters for the production of metals. Lead operations are many times integrated with zinc operations, as in the Teck Cominco, Trail operations, described in Section 3.2.

Globally, about 80% of the lead production is based on the blast furnace process and 10% on the imperial smelting process. Other processing routes (e.g., Kivcet ''flash'' furnace), account for the balance of the global production.

Most lead smelters are designed to treat a wide range of feed materials including lead concentrates, residues from the zinc plants, recycled lead battery scrap, and scrap copper [17]. Blast furnaces are described in the copper section. Below we summarize the newer flash furnace, which eliminates the need for sintering and significantly reduces dust and fume emissions. The lead concentrates are heated in a furnace with oxygen, silica and limestone for fluxing, residues from other plants (e.g., zinc) recycled battery scrap, and dry fine coal for fuel. The sulfur in the concentrates and the fine coal ignite instantly, forming sulfur dioxide and oxides of lead, zinc, iron and minor metals. The fluxing agents and the oxides form a slag, the burning coke floats at the top of the molten slag, and the metal oxides percolate though to form metal bullion at the bottom. The bullion is further processed through a drossing furnace to remove and recover copper, arsenic and antimony. After this

Table 5
Estimated life cycle inventory of energy and emissions for mining and smelting/refining stages of Zn and co-products

| | Allocation criteria | | | |
|---|---|---|---|---|
| | Mass[a] | Economic value[b] | | |
| | Zn/Cd/In/Ge/Ga | Zn | Cd | In |
| Energy (GJ/tonne) | | | | |
| Mining[c] | | | | |
| Electricity | 4.2 | 3.2 | 1.3 | 450 |
| Fuel oil | 6.0 | 4.6 | 1.8 | 640 |
| Smelting/refining[d] | | | | |
| Electricity | 6.3 | 4.8 | 1.9 | 680 |
| Coal | 3.2 | 2.4 | 0.9 | 340 |
| Natural gas | 8.4 | 6.4 | 2.5 | 900 |
| Fuel oil | 1.3 | 1.0 | 0.4 | 140 |
| Emissions to air (g/tonne) | | | | |
| Mining | | | | |
| Particulate | 60 | 46 | 18 | 6400 |
| Smelting/refining[a] | | | | |
| $SO_2$ | 14,400 | 10,900 | 4300 | 1,535,000 |
| As | 5.1 | 3.9 | 1.5 | 550 |
| Cd | 2.0 | 1.5 | 0.59 | 210 |
| Cr | 0.90 | 0.68 | 0.27 | 96 |
| Co | 0.15 | 0.12 | 0.045 | 16 |
| Cu | 238.9 | 182.0 | 71.2 | 25,500 |
| Pb | 104.3 | 79.6 | 31.1 | 11,200 |
| Hg | <0.04 | <0.03 | <0.01 | <400 |
| Ni | 0.88 | 0.67 | 0.26 | 94 |
| Ag | 0.86 | 0.65 | 0.26 | 92 |
| Zn | 129.7 | 98.9 | 38.7 | 13,900 |
| Emissions to water (g/tonne) | | | | |
| Mining | N/A | N/A | N/A | N/A |
| Smelting/refining | | | | |
| As | 0.35 | 0.27 | 0.10 | 37 |
| Cd | 0.58 | 0.44 | 0.17 | 61 |
| Cr | 0.12 | 0.09 | 0.04 | 13 |
| Co | 0.73 | 0.55 | 0.22 | 78 |
| Cu | 3.6 | 2.7 | 1.1 | 380 |
| Pb | 0.60 | 0.46 | 0.18 | 64 |
| Ni | 0.65 | 0.5 | 0.2 | 70 |
| Ag | 0.12 | 0.09 | 0.04 | 13 |
| Zn | 74.3 | 56.8 | 22.2 | 7960 |

[a] Estimated from [21].
[b] Estimated from [40–42].
[c] Assuming 3% zinc ore, based on mostly underground mining, i.e., 25 of 27 lead/zinc mines in 1997 [38].
[d] Data for CEZ, energy composition is estimated from [39].

purification, the bullion is poured into ingots and transferred to the lead refinery for electro-refining, which produces slimes that are treated in a series of furnaces to recover silver, gold and bismuth. The purified bullion is then cast into the finished products. The lighter slag is transferred to a slag furnace to remove zinc, mainly in the form of a zinc oxide fume. The fume is processed in the leaching plants in zinc operations to extract more zinc. The remaining ''ferrous granules'' (black sand-like slag) is sold to cement manufacturers.

Energy is recovered from the hot emissions by passing the gasses through a heat exchanger, while an electrostatic precipitator removes the particles. The $SO_2$ emissions then are processed into sulfur products (e.g., sulfuric acid and liquid sulfur dioxide) [17].

Emissions of Cd from lead smelters are tabulated by Fthenakis [13]. Cadmium from all sources range from 0.6 g/tonne product for plants with cyclones and ESPs, to 22 g/tonne product for plants with limited emissions abatement.

## 4. Production of copper and co-products (Mo, Se, and Te)

### 4.1. Mining and beneficiation

Copper is found in many minerals such as cuprite ($Cu_2O$), malachite ($CuCO_3{\cdot}Cu(OH)_2$), azurite ($2CuCO_3{\cdot}Cu(OH)_2$), chalcopyrite ($CuFeS_2$), and bornite ($Cu_5FeS_4$). The most important copper ores are the sulfides and oxides. Globally, about 80–90% of the primary copper production is derived from sulfide ores [43], the balance is derived from oxide ores. The copper ores are of low grade, often less than 1% Cu. Copper from currently mined ores averages around 0.8% in grade globally. In addition to its primary production, copper is also produced by recycled scraps (secondary production). In 2001, copper recovered from all refined or re-melted scrap composed 34% of the total US copper supply [44] and in 2003 this contribution was 31% of the US copper supply [45]. The worldwide land-based resources are estimated to be 1.6 billion tonnes of copper, and resources in deep-sea nodules are estimated to be 700 million tonnes. In the United States, discovered resources are estimated to contain 350 million - tonnes of copper, and undiscovered deposits are estimated to contain 290 million tonnes of copper [45]. Major mining operations are located in the United States, Chile, Peru, Mexico and Canada. The ores are mined in both open pits and underground mines, depending upon the ore grade and the nature of the ore deposit. Once the ore is delivered above the ground, it is crushed, ground and concentrated (beneficiated) for further processing. In the beneficiation process, ground ore is slurried with water, chemical reagents (e.g., xanthates, alcohols, and pine oil) are added, and air is blown through the slurry. The air bubbles attach themselves to the copper minerals and are then skimmed off of the top of the flotation cells. The concentrate contains between 20% and 30% copper. The ''tailings,'' or gangue minerals, from the ore fall to the bottom of the cells are removed, dewatered by ''thickeners,'' and transported as a slurry to a tailings pond for disposal. All water used in this operation, from dewatering thickeners and the tailings pond, is recovered and recycled back into the process [46].

### 4.2. Copper production

Copper is produced either pyrometallurgically or hydrometallurgically depending upon the ore-type. Concentrates produced from copper sulfide ores are treated by pyrometallurgical processes, whereas those from copper oxide ores, are usually treated by hydrometallurgical processes together

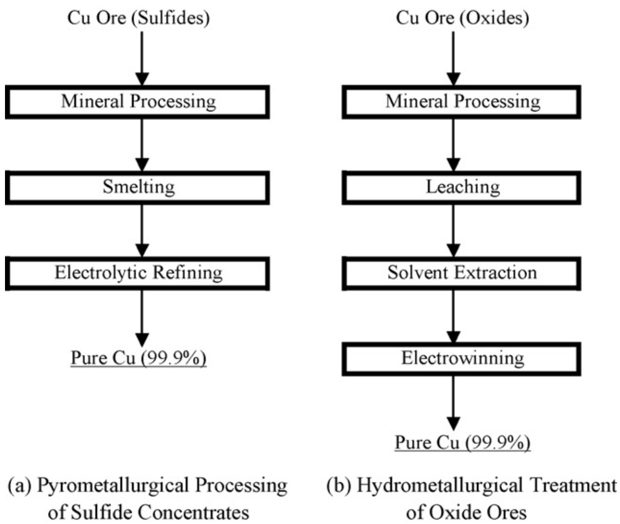



Fig. 8. Extractive metallurgy of copper.

with oxidized waste materials. The pyrometallurgy of copper is a multistage process, beginning with the mining and concentrating of low-grade ores containing copper sulfide minerals, and followed by smelting and electrolytic refining to produce a pure copper cathode. About 80% of the world's primary copper is produced from sulfide ores such as chalcopyrite ($CuFeS_2$). The hydrometallurgical route, known as leaching–solvent extraction–electrowinning (SX–EW), involves leaching, solvent extraction, and recovery by precipitation or electrowinning. In the United States, about 70% of domestic primary refined copper is produced from a multistage process, beginning with the mining and concentrating of ores, and followed by smelting and electrolytic refining to produce a high-grade copper cathode. The rest 30% is produced from acid leaching of copper ores and wastes and solvent extraction and electrowinning of refined copper from the pregnant solution. A general flowchart for the extractive metallurgy of copper is shown in Fig. 8.

#### 4.2.1. Pyrometallurgical processing

Pyrometallurgical processes employ high-temperature chemical reactions to extract copper from its ores and concentrates. The traditional pyrometallurgical copper-smelting process is schematically shown in Fig. 9. Generally, these processes are used with low-grade or poor copper sulfides and, in some cases, high-grade oxides. Depending on the copper mineral and the type of equipment, pyrometallurgical processing from copper concentrates follows the following sequence [43,47–49].

*4.2.1.1. Roasting.* The purpose of the roasting is to decrease the sulfur content to an optimum level prior to form copper. Roasting is a process to convert copper and iron sulfide concentrates (25–30% Cu) to oxides, thereby removing most of the sulfur (as sulfur dioxide). Two main types of furnaces have been used, viz., multiple hearths, and fluidized-bed roasters. In modern copper smelters, roasting has been abandoned as a separate step and has been combined with the smelting furnace.

*4.2.1.2. Smelting.* Smelting involves the application of heat to a charge of copper ore concentrate, scraps, and flux to fuse the ore and allow the separation of copper from iron and other impurities. Modern copper-smelting furnaces accommodate both roasting and smelting operations in one unit. There are

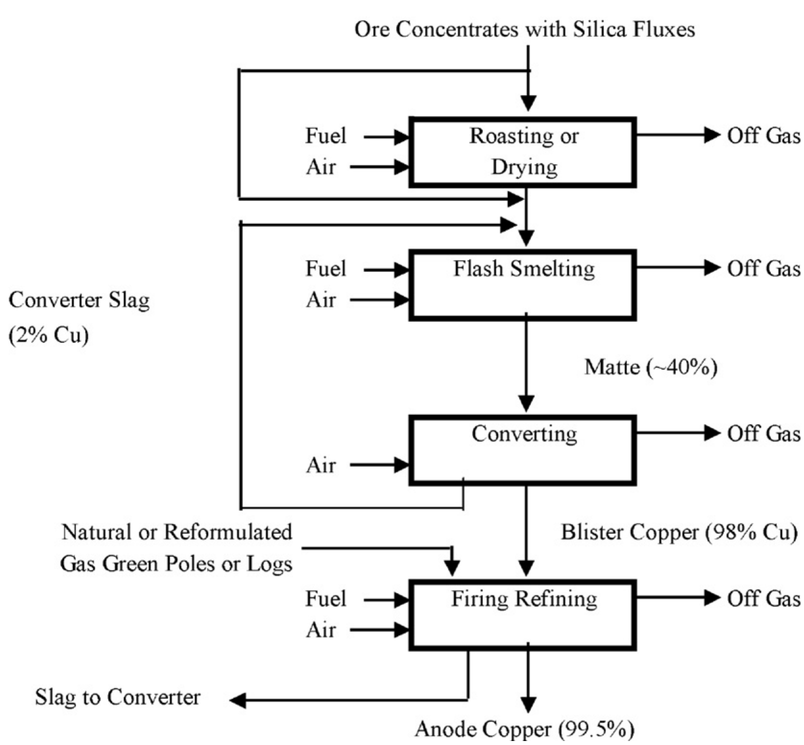



Fig. 9. Typical primary copper smelter process [50].

four major types of copper smelters in use, namely reverberatory furnaces, electric furnaces, flash smelters and bath smelters. The first two are essentially batch-type and consequently inherently less efficient than the latter two types. Therefore, the latter two are more and more widely used. Flash smelting employs oxygen-rich air to promote autogenous conditions while bath smelting is dependent upon the roasting and smelting steps occurring within a molten pool containing both matte and slag phases. There are two types of flash smelters, the Outokumpu and INCO systems. In both cases a finely divided dry concentrate is fed into a hearth-type furnace. The Outokumpu flash smelting process combines the conventional operations of roasting, smelting and partial converting into one process. Preheated oxygen-enriched air (about 25% $O_2$) is used to provide heat so that additional fuel is not required for the reactions to proceed. Copper concentrate is recovered from the slag and recycled through the smelter. The clean slag is sent for disposal. Heat and particulates are recovered from the smelter gases using baghouses and wet scrubbers, and the collected residues are recycled in the smelter. Gaseous stream containing 10–30% of $SO_2$ is used for production of sulfuric acid. The matte is further treated in conventional converters to obtain blister copper. The main advantages of the Outokumpu process are the high sulfur recovery, the efficient energy utilization, and the flexible process in terms of accepting a varied feed material. Energy consumption for the new technology is about 20–30% of that required with a conventional furnace. Fifty to 80% of sulfur is recovered from the concentrate for use in sulfuric acid production, reducing $SO_2$ emissions to the environment. Slag cleaning reduces copper content from 24% to less than 0.6% prior to disposal, eliminating problems due to liquid run-off from granulation pond. This process utilizes dry copper concentrates. This process, developed by Outokumpu Technology Oy, produces half of the world's primary copper. The flowsheet of Outokumpu's flash smelting process [51] is shown in Fig. 12. The INCO design, introduced in 1983, utilizes pure oxygen and yields a gas stream that is 80% $SO_2$. The worldwide large smelters such as Kennecott Utah copper smelter in USA, Boliden's Rönnskär smelter in Sweden, Olympic Dam in South Australia use Outokumpu's flash smelting process.

Bath smelters include the Noranda and the Mitsubishi systems. The Noranda system employs a refractory-lined cylindrical vessel to smelt a broad range of copper-bearing materials (e.g., sulfide concentrate, inerts, scraps, and recycled substances). The Noranda submerged tuyere rotatable furnace design combines the functions of roaster, smelter and partial converter. An example of the Noranda process is the Horne smelter in Rouyn-Noranda, Quebec, Canada. It has the capacity to process 850,000 tonnes of materials per year, yielding 220,000 tonnes of copper anode and 500,000 tonnes of sulfuric acid. Until the 1970s, this smelter utilized conventional copper-smelting technology, which included reverberatory furnaces and Peirce-Smith converters. Upgraded in late 1990s, it is now the largest and most advanced recycling plant of its kind in North America. Another important bath smelting technology is the Mitsubishi continuous smelting and converting process. It combines roasting, smelting and converting (e.g., oxidizing) in a continuous operation enabled by three furnace units (smelting, slag cleaning, and converting) interconnected via heated and covered launders. Two separate molten streams are generated in smelting: copper–iron sulfide matte and slag in addition to off-gas rich in sulfur dioxide. The high-grade mattes may contain as much as 75–80% Cu and up to 1% Fe, which is further treated by a converter (it is a furnace widely used in steel making and copper making process). The slag phase is composed of silicates enriched in iron. The off-gas is sent to acid plant for sulfuric acid production. The Falconbridge Kidd Creek copper smelter in Canada utilizes the Mitsubishi process [52].

*4.2.1.3. Converter smelting.* The matte generated from flash smelting furnace is then transferred to a converter where copper sulfide is oxidized to metallic copper. In a converter, oxygen-enriched air is blown into the furnace. The product of a converter is called blister copper that averages 98–99% Cu and about 0.02–0.1% S. The off-gas is rich of sulfur dioxide, which is sent to acid plant. There are two main types of batch converters, the Pierce-Smith (the most common) and the Hoboken system.

There are three types of continuous converter: flash converting, lance converting, and submerged tuyere converting. All three offer better control over oxygen intake than batch converters and generate concentrated sulfur dioxide, which is easily captured for acid production. The continuous flash converter uses finely ground solid matte from an Outukumpu flash furnace. This process is used in Kennecott's facility in Utah [53].

The other two continuous converters utilize liquid matte, which is thermodynamically preferable to batch conversion. The first continuous lance converter was the Mitsubishi continuous converter.

*4.2.1.4. Fire refining.* Fire refining is usually carried out prior to the electrolysis of copper. The fire refining is operated in either reverberatory or rotary furnaces known as anode furnaces. Through this step, oxygen and other impurities in the blister copper can be removed before the copper is cast into anode for electrolytic refining. The processed blister copper, also known as copper anode is cast into anode shapes. Impurities are oxidized and reported to slag phase. Precious metals are not oxidized and remain in the host metal until later recovered during electrolytic operations. The purity of copper anode varies from 99% Cu to 99.6% Cu.

*4.2.1.5. Electrolytic refining.* In electrolytic refining, the copper anodes produced from fire refining are taken to a "tank house", where they are dissolved electrolytically in acidic copper sulfate solution. This electrolyte solution usually has the composition of Cu 40–50 g/L; $H_2SO_4$ 170–200 g/L; $Cl^-$ 0.02–0.05 g/L. The produced cathode copper has a purity of 99.97–99.99% Cu. The insoluble anode slim is collected for the recovery of precious metals.

Although copper was recovered at 22 mines operating in the United States, just 13 mines accounted for more than 99% of

production. Three primary smelters, 4 electrolytic and 3 fire refineries, and 12 solvent extraction–electrowinning facilities operated during the year 2003 [45]. Because of increasing use of $H_2SO_4$ for the SX–EW process, the US smelters use all the $H_2SO_4$ they produce and also import some [43]. (In US, Phelps Dodge is the only major producer of copper using both pyro- and hydromethods. Other producers use pyromethod. Electrolytic refining of copper also consumes $H_2SO_4$.)

In Chile, the largest copper producer in the world, sulfur fixation was only about 70% as of late 1990s; more recent data are not available.

*4.2.2. Hydrometallurgical processing*

Hydrometallurgical copper recovery is the extraction and recovery of copper from ores using aqueous solutions [47–49]. Because of this, this route is also called solution method. Oxide ores and supergene sulfide ores, i.e., ores not containing iron, can be recovered most easily by hydrometallurgical techniques [43]. The hydrometallurgical approach basically consists of two major operation units, which are leaching and precipitation.

*4.2.2.1. Leaching.* In hydrometallurgical process, the leaching process extracts copper by dissolution in ammonia, sulfuric acid, or hydrochloric acid. This process can operate at atmospheric pressure or as pressure leach circuits. This method is suitable for low-grade copper ore bodies for which customary mining operations would be uneconomical, as well as for the leaching of remnant ores from abandon mines. The leaching methods include dump, heap, and vat leaching techniques, as well as underground (or in situ) leaching methods.

Dump leaching is used to recover copper from large quantities (millions of tonnes) of strip mine waste with a very low grade. Copper recovery rates vary from 30% to 70% [43]. Heap leaching is essentially the same as dump leaching, except that it is applied to oxide ores. Recovery of 70–80% is possible by heap leaching. In vat leaching, oxide ores are crushed and placed in large concrete vats (up to 18,000 tonnes capacity), then flooded by concentrated sulfuric acid, which converts most of the copper to copper sulfate. Extraction of 1 tonne of copper from ore with a grade of 1% requires 4400 l of 96% sulfuric acid. A vat leaching typically recovers 75% of the copper. The process is fairly rapid (hours to days).

Leaching of ores and concentrates is limited to acid-soluble ore oxides that are not associated with calcite rock that consumes acid. In practice, the process is most commonly used for leaching low-grade deposits in situ or as heaps. A variety of techniques are used to extract copper—some ore is roasted or calcified before leaching, while other ore is subjected to microbial leaching. Microbial (or bacterial) leaching is used for low-grade sulfide ores; however, this type of leaching is much slower than standard acid leaching. Its application is still in pilot scale and commercial production is reported with this method.

*4.2.2.2. Precipitation or SX/EW.* Once the copper is extracted into liquid phase, it can be then removed from the pregnant

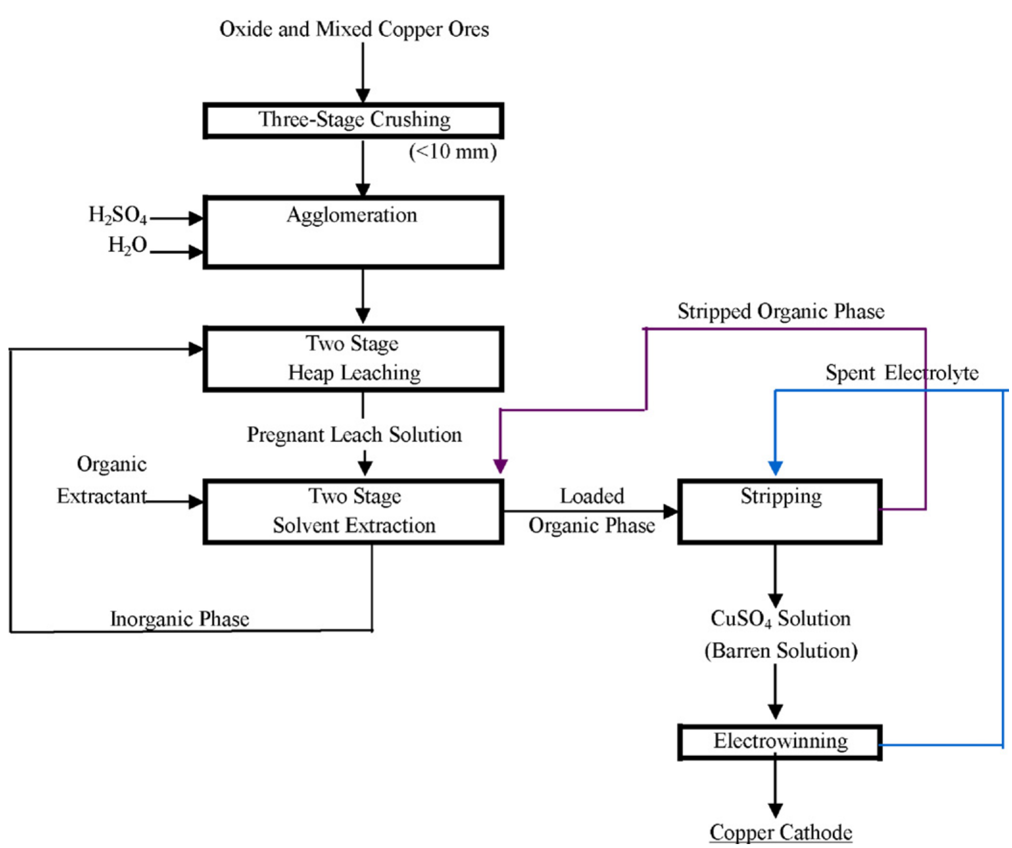



Fig. 10. SX/EW plant flowsheet of the copper operation facilities at Collahuasi in northern Chile [54].

leachate through either precipitation (or cementation) or solvent extraction and electrowinning (SX/EX).

In cementation, once the most popular method for recovering copper from the pregnant leachate, the leachate is combined with de-tinned iron in scrap iron or cementation mill where the iron replaces the copper in the solution. The copper precipitates are removed for subsequent pyrometallurgical processing. The product of cementation is cement copper.

The leaching–cementation process has now been almost universally overtaken by solvent extraction. Agitation leaching with solvent extraction is a method to produce a relatively pure solution of copper sulfate suitable for electrowinning.

In solvent extraction, now the most popular process, an organic chemical (chelating agent) that binds copper but not impurity metals is dissolved in an organic solvent (often kerosene). The chemical is then mixed with the pregnant leach solution. The organic solvent is separated in a settler and stripped with concentrated sulfuric acid to produce a clean, high-grade solution of copper for electrowinning. The barren leachate (or raffinate) is sent back to the leaching system.

*4.2.2.3. Electrowinning.* Electrowinning is the electrodeposition of copper from the loaded electrolyte solution produced by solvent extraction, yielding refined copper metal. The electrowinning is functionally equivalent to electrolytic refining, but differs in that electrowinning uses a permanent, insoluble anode. The depleted electrolyte from electrowinning is returned to the SX plant. Excess depleted electrolyte from the SX unit is returned to the raffinate pond to be recycled into the leaching circuit. Filter clay is used to filter the electrolyte. Impurities left on the bottom of the electrowinning cells are called ''anode mud''. Both this anode sludge and lead anodes that are no longer usable are periodically removed from the cells and sent to lead-smelting facilities for resource recovery. The electricity requirement is quite high because a comparatively high voltage is needed (3.0 volt) comparing to electrorefining. The product of the SX/EW is copper cathode with purity of 99.95–99.99% Cu [54]. The solvent extraction–electrowinning (SX–EW) plant flowsheet of the Falconbridge Limited's copper operation facilities at Collahuasi in Chile is shown in Fig. 10. This plant produced a total of 27,895 tonnes of copper in 2003. The SX/EW process differs from traditional electrolytic refining in that the anodes are inert (Pb–Sn–Ca). The copper is deposited on the cathode, liberating oxygen and regenerating the sulfate ion as sulfuric acid. Implementation of the SX/EW process is growing and is displacing the older pyrometallurgical approach. However, whereas the pyrometallurgical approach is a net producer of by-product sulfuric acid, the hydrometallurgical process is a net consumer of the acid. Thus, in the long run it is likely that the two will be increasingly combined [43]. The SX/EW process has been used by Phelps Dodge Mining Co. in USA [55].

### 4.3. Selenium production

Selenium is a rare element widely distributed within the earth's crust, which like In, Ga and Cd does not occur in concentrations high enough to justify mining solely for its content. It is recovered as a by-product, mostly from the anode slimes in the electrolytic refining of copper. An estimated 41,000 tonnes of wet copper anode slimes are generated annually, with about 17% of these being produced at refineries without equipment for processing them [56]. Slimes resulting from primary metal refining can have average selenium concentrations of about 10%, increasing to as high as 40% in a few cases. Coal contains an average of 1.5 ppm of selenium, which is about 80 times the average of copper deposits, but recovery of selenium from coal appears unlikely in the foreseeable future because of the high volatility of the element [57].

About 250 tonnes of secondary selenium is produced every year worldwide. This represents about 15% of refined selenium production coming from secondary sources. World refinery production of primary selenium (excluding US production) increased less than 1% to 1480 tonnes in 2002. Japanese output, which accounted for approximately 50% of the world total, is reported to have increased by 1% to 740 tonnes. Belgium, Canada, Japan, and the United States represent over 80% of the total world refinery production of selenium and tellurium [56,58].

In the United States, only one domestic copper refinery recovers and produces high-purity selenium (99.999%)—ASARCO Incorporated, Amarillo, TX. One domestic producer exported semi-refined selenium (90% selenium content) for refining in Asia. Three other companies generated selenium-containing slimes, but did not produce selenium. Selenium-containing slimes from these refineries were exported for processing.

In Canada, primary selenium is recovered as a by-product from copper refining from two smelters. Noranda Metallurgy Inc. produces commercial and high-purity selenium at its CCR refinery in Montréal, and Inco Limited produces crude selenium at its Copper Cliff copper refinery in Sudbury.

Selenium is present in the anode slimes of electrolytic copper refining, which are those constituents in the copper anodes that are not solubilized during the electrolytic refining process and accumulate at the bottom of the electro-refining tank [59]. These slimes contain ~10% selenium and ~5% tellurium. The slimes contain 25–70% of the selenium content of the copper ore; the rest vaporizes during smelting [60]. The slimes are treated primarily for value of the precious metals gold, silver, platinum, palladium, and rhodium they contain. The recovery of selenium is a secondary priority [59].

Two major processes of extracting selenium from copper refinery slime include roasting with soda ash and roasting with sulfuric acid (Outokumpu Oy Process). Other methods include wet chlorination, oxidative leaching with sodium hydroxide solution under pressure, hydrometallurgical process of chlorination in hydrochloric acid, etc. [59,60].

Soda ash roasting is a traditional method to recover selenium and tellurium commercially. With aeration, soda ash is used to convert selenium and tellurium into a 6+ oxidation state. Electrolytic copper refinery slimes are intensely mixed with

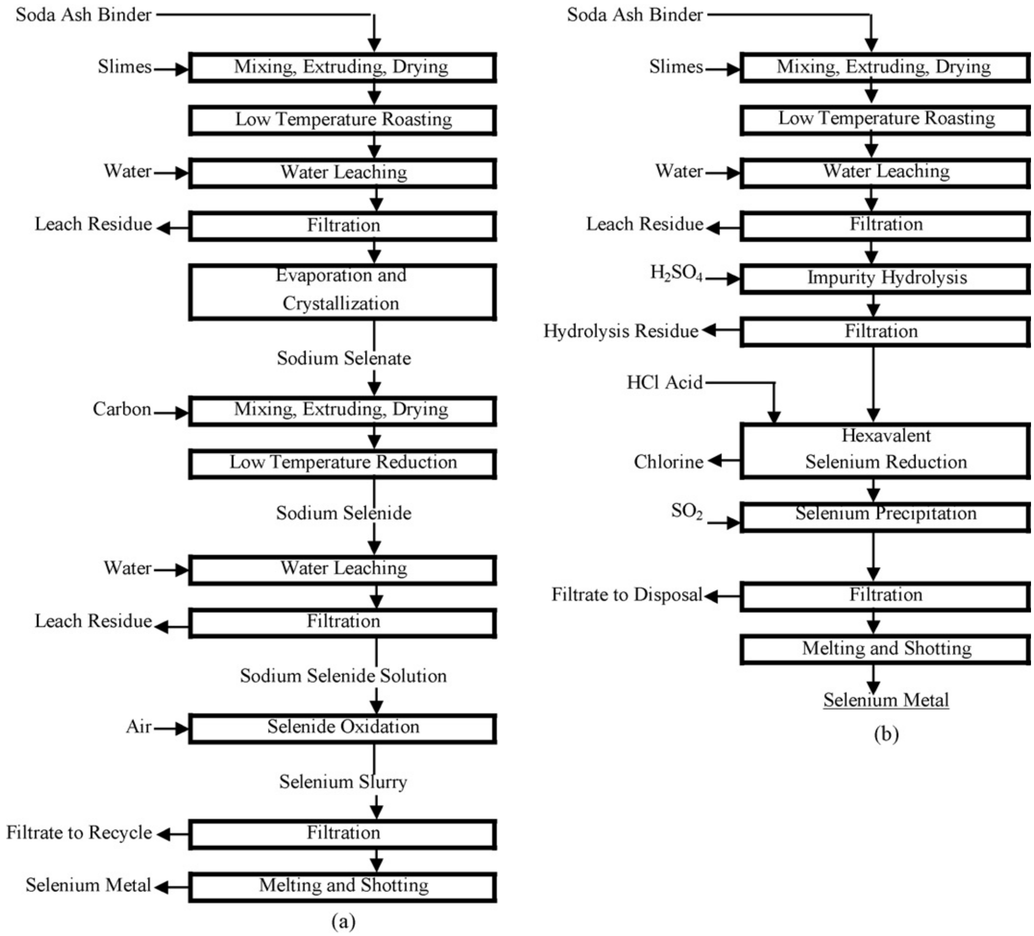



Fig. 11. Recovery of selenium by soda ash or sodium carbonate roasting of slime [61].

soda ash binder, or sodium carbonate, and water to form a paste, which then palletized [59]. The pellets are roasted at roasting at 530–650 °C, are ground into powder and leached in water to dissolve sodium selenate. Sodium tellurate is insoluble in the alkaline leaching solution, so it is separated from the selenate with filtration. The tellurate-bearing residue is treated separately.

Recovery of selenium from the sodium selenate solution can be accomplished in two ways. First, the selenate is crystallized from solution [60]. Then charcoal, or carbon, is added to the crystalline hexavalent sodium selenate, and after mixing, heating and drying, it is reduced to sodium selenide. The dry sodium selenide is leached with water and filtered to form a concentrated solution of sodium selenide. The selenide is oxidized as air is blown through the solution to get selenium slurry. Again precipitation occurs in which much of the solution could be recycled back into the process. The precipitate undergoes melting and shotting before selenium metals is attained. Shotting is described as ''passing molten metal through a sieve and dropping particles into water [61]'' (see Fig. 11).

The second path uses sulfuric acid to remove many of the impurities in hydrolysis. Filtration occurs to remove the hydrolysis residue. Hydrochloric acid or ferrous iron salt is used for the reduction of hexavalent selenium. Iron chloride is discarded, which contain small amounts of selenium but is also extremely corrosive and creates problems for disposal. The remaining solution is precipitated with sulfur dioxide and then filtrated. Similarly, the final steps are melting and shotting to produce selenium metal (see Fig. 11).

Another important recovery process is the Outokumpu process, which is practiced at Harjavalta, Finland [51]. The flowsheet of precious metal recovery at Outokumpu Harjavalta Metals Oy is shown in Fig. 12. As described before, the anode slime mainly contains elements electrochemically nobler than copper (Te, Se, Ag, Au, Pt, and Pd). The slime slurry is pumped electrolysis to the precious metals plant.

The slime is first leached in an autoclave at 170 °C with 6–7.5 bar oxygen pressure in order to dissolve nickel, copper and tellurium. Tellurium is precipitated from the solution as copper telluride and sold in this form.

Selenium is recovered from the filter press cake in an electrically heated furnace where the temperature is kept at around 400–600 °C. Oxygen and $SO_2$ gas are used as reagents. Selenium compounds react at this temperature forming gaseous selenium dioxide. The selenium dioxide gas ($SeO_2(g)$), is sucked from the furnace through the ejector into an aqueous solution. In this solution selenium dioxide is reduced to elemental selenium by sulfur dioxide at the temperature of 80 °C. The selenium is commercial grade selenium (>99.5%). Selenium recovery is high. The selenium content of the roasted slime is normally around 0.5%.

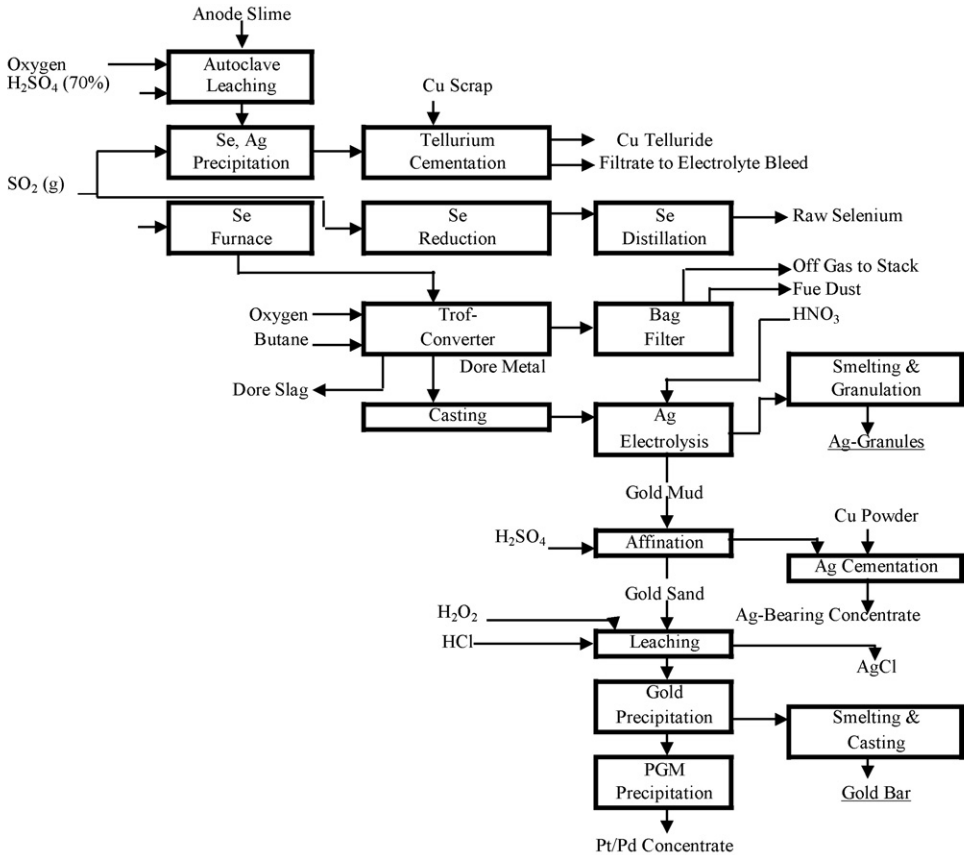



Fig. 12. Recovery of selenium from copper anode slime by Outokumpu process [51].

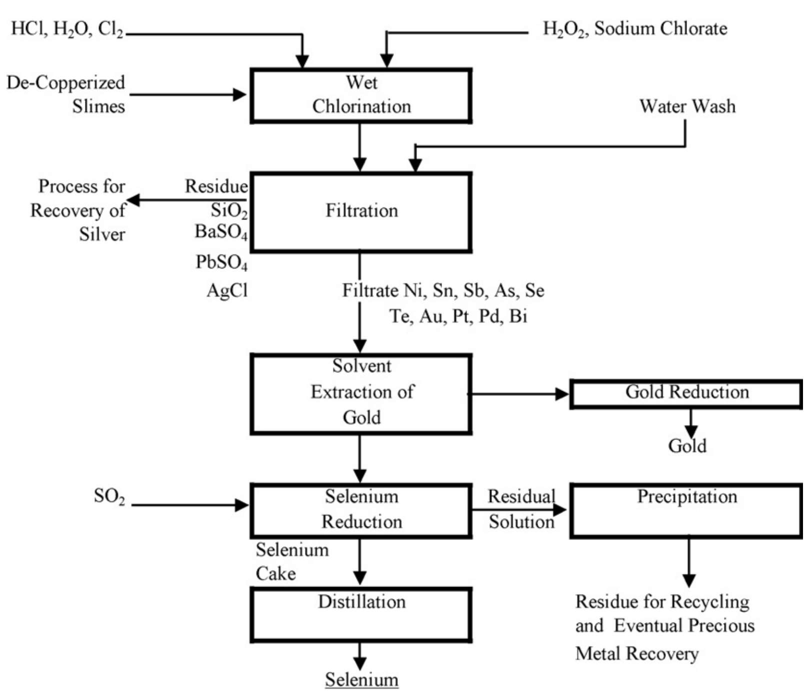



Fig. 13. Recovery of selenium by wet chlorination [59].

Due to the fact that the roaster is furnished with gas circulation devices, it offers homogenous atmospheric conditions throughout the roaster, which leads to nearly complete removal of selenium during the process. The remaining aqueous solution is fed back to copper electrolysis.

Wet chlorination process is a rapid and simple process of "obtaining high extractions of selenium from slimes [59]." In 1995, the Kennecott Utah Copper Corporation (KUCC) was the first to use wet chlorination of slimes to recover selenium and other metals. In wet chlorination, refinery slimes slurried in water or hydrochloric acid are sprayed or sprinkled with chlorine gas. In some cases, other oxidants are used such as sodium chlorate or hydrogen peroxide, which liberate chlorine from hydrochloric acid at about 100 °C [59]. Some selenium and selenide oxidizes and dissolve in the solution, but it is negligible. The main residues removed are $SiO_2$, $BaSO_4$, $PbSO_4$ and AgCl, and silver is usually recovered from it. The filtrate, which includes nickel, tin, antimony, arsenic, selenium, tellurium, gold, platinum, palladium, and bismuth, is then processed to extract the gold. Once the gold is removed, the chlorination liquor is reduced with sulfur dioxide to recover selenium and other precious metals. The acidity, temperature, and rate of reduction are carefully controlled. After the selenium is reduced, the residual solution is precipitated for precious metals. As for the selenium cake, vacuum distillation is used to recover pure selenium (see Fig. 13).

After selenium is extracted from copper refinery slimes, the average purity of the selenium is approximately 99%. For photovoltaics, a slightly higher purity of 99.99% is preferred. The simplest and the most common method of achieving 99.99% pure selenium is vacuum distillation. When distillation is performed under a vacuum, there are less emission problems, improved separation, and less corrosivity. Many of the impurities such as sulfur dioxide, water, organic matter, halogens, sulfuric acid, and mercury are all sent to a scrubber.

During the distillation, "all the nonvolatile elements, such as copper, nickel, iron, and tellurium remain in the distillation vessel. However, sulfur and mercury also distill over and are thus not removed [60]." Therefore, crude selenium is free of mercury and many other impurities.

There are two other methods of purifying crude selenium. First is to vaporize the selenium with oxygen to form selenium dioxide, which could be absorbed in pure water. "Mercury can be removed from the solution by adsorption, and the other metallic ions by ion exchangers. Elemental selenium is then precipitated with high-purity sulfur dioxide [60]" to achieve a purity of >99.99%. Second is to dissolve the selenium in sodium sulfite, and filter it. Many impurities will not dissolve and will be filtered out, while the remaining filtrate "is acidified with sulfuric acid to precipitate selenium [62]." Lastly, the selenium is distilled to remove the impurities to produce high-purity selenium.

### 4.4. Tellurium production

Tellurium is a rare metal that can be extracted as by-product of processing copper, lead, gold, and bismuth ores. In 1982 about 90% of tellurium was recovered from the slimes formed during the electrolytic refining of copper [63]. The slimes contain copper, tellurium, selenium, and other metals. Copper typically is removed by oxidative pressure leaching with dilute sulfuric acid at 80–160 °C. This completely extracts the Cu, and removes 50–80% of the Te according to one source [64] or more than 90% according to another [65]. The range of Te extraction is wide because its concentration in slimes varies significantly. Tellurium is recovered from solution by cementation with copper. Copper telluride is leached with caustic soda and air to produce a sodium telluride solution. The latter is used as the feed for producing commercial grade Te metal or $TeO_2$. Both of these forms can be used in CdTe formation for solar cells.

Asarco in the United States produces commercial grade tellurium at its refinery complex in Amarillo mainly from two sources: copper anode slimes and lead refinery skimmings [66]. However, the production level is not available.

In Canada, primary tellurium is recovered as a by-product from copper refining. Noranda Metallurgy Inc. produces commercial and high-purity tellurium at its CCR refinery and Inco Limited produces crude tellurium at its Copper Cliff copper refinery.

### 4.5. Molybdenum production

About 50% of the global supply of molybdenum is produced as a co-product or as a by-product of copper mining. The rest is obtained by dedicated (primary) mining. In co-product mining commercial viability is dependent upon the extraction of both molybdenite and copper-bearing minerals, whereas in by-product mining molybdenite is obtained during copper recovery.

Molybdenum is produced as a by-product of copper production at the Bagdad and Sierrita Mines in Arizona (operated by Phelps Dodge Corp., as copper–molybdenum ore, concentrated with a total concentrate molybdenum production of 29,747,000 lbs in 2003) [55] and at the Bingham Canyon Mine in Utah (operated by Kennecott Utah Copper Corporation, as copper–molybdenum ore, concentrated). Two roasting plants converted molybdenite ($MoS_2$) concentrate to molybdic oxide, from which intermediate products, such as ferromolybdenum, metal powder, and various chemicals, were produced. (The data shown in this section refer to the contained molybdenum in concentrate, in average, Mo 48–58.8% contained in unroasted concentrate.)

Kennecott Utah Copper Corporation (KUCC) recovers molybdenum as a by-product at its copper concentrator. However, the production of molybdenum at KUCC fell by about 28% year on year to 4600 tonnes in 2003 owing to reduced ore grade. Approximately 8180 tonnes of molybdenum are recovered each year through the flotation process at KUCC.

At KUCC, the molybdenum is recovered in the following procedures [67]: In copper beneficiation process, once the copper ore emerges from the concentrator as a fine powder, it is put through a series of flotations. Then chemicals and liquids are applied to the powder so that all the copper, gold, silver, and molybdenum float to the top of the flotation cells in frothy

Table 6
Uncontrolled emissions from metallurgical operations [69]

| Metal | Steel and foundries (ppm) | Smelt/refine copper (ppm) | Smelt/refine lead (ppm) |
|---|---|---|---|
| Arsenic | 15.2 | 8000 (refinery 800–900) | |
| Cadmium | 3.5–4.0 | 350–650 | 1750–2100 |
| Chromium | 6.5–7.0 | – | – |
| Copper | 17.5–22.5 | 2500–5000 | – |
| Mercury | – | 26 air 1 water | 9 air 0.5 water |
| Lead | 200–300 | 2000–5000 (refinery 25) | 20,000–23,000 |
| Zinc | 27–370 | 9000–11,000 | 500–100 |

bubbles, which are skimmed off. This is done a few more times, so that finally the molybdenum disulfide is floated off. This rough concentrate goes through its own flotation circuit, for further cleaning. At the end of the production cycle, it ends up with a high quality moly concentrate—molybdenum disulfide, which is about 55% molybdenum. At this point, the molybdenum disulfide concentrate is shipped to roasting facilities, which further process the concentrate into the finished product—molybdic oxide, which is sold to steel mills all over the world.

Molybdenite recovery from copper circuits at porphyry copper mines accounts for 75% of the Western and 50% of worldwide molybdenum supply. In 2003, The US mine production of molybdenum concentrate was 32,000 tonnes in 2002 and 33,500 tonnes in 2003. The world's primary production of molybdenum was 121,000 tonnes in 2002, and 125,000 tonnes in 2003 [68].

### *4.6. Emission factors in the co-production of Cu, Mo, Se, and Te*

Crushing and grinding of ores in copper mines generates dust emissions at the same levels as those in mining zinc ores (discussed in Section 3.1). Solid wastes in mining comprise the biggest solid waste contributor in the life cycle of the metals. In addition to the ore itself, a large amount of waste rock (overburden) is removed to get access to the ore, especially in surface mines. The ratio of overburden to concentrator mill tailings in the US is now about 1.9:1 [43]. The most serious environmental problem associated with copper mining is acid rock drainage, formerly known as acid mine drainage, and largely associated with coal mining [43].

Table 7
Typical $SO_2$ concentration in off-gas from primary copper smelters [70] (after Pacyna)

| Process unit | $SO_2$ concentration (vol.%) |
|---|---|
| Multiple hearth roaster | 1.5–3 |
| Fluidized-bed roaster | 10–12 |
| Reverberatory furnace | 0.5–1.5 |
| Electric arc furnace | 4–8 |
| Flash smelting furnace | 10–70 |
| Continuous smelting furnace | 5–15 |
| Pierce-Smith converter | 4–7 |
| Hoboken converter | 8 |
| Single contact $H_2SO_4$ plant | 0.2–0.26 |
| Double contact $H_2SO_4$ plant | 0.05 |

The second largest solid waste component consists of mill tailings or gangue, which is un-mineralized rock separated from the mineralized concentrate during the beneficiation process. The global average is 37 tonnes waste/tonne of concentrate [43].

The next stage of waste generation occurs at the smelter/converter. Smelter recovery of copper from concentrate averages 98%. About 2% of the copper (and some sulfur) remains in the slag. The slag amounts to about 1.55 tonnes/tonne copper assuming concentrate with a grade of 25%.

Gaseous emissions generated from primary copper smelters include sulfur dioxide and particulates from the roasters, smelting furnace, and converters. Copper and iron oxides are the primary constituents of the particulate matter; other constituents include the oxides of arsenic, antimony, cadmium, lead, mercury, and zinc. There are eight copper smelters in the United States. Sulfur dioxide is recovered in the form of sulfuric acid in all but one of these smelters. Particulate emissions are treated in ESPs or combination spray/ESP systems with efficiencies of 95–99%. The emissions from copper smelting can vary widely depending on the ore used and the abatement measures applied. We found no explicit quantification of cadmium emissions in copper smelting in the literature. Indirect estimates can be made from comparing the Cd concentrations in copper and lead smelters. Table 6 shows those compiled by Ayres and Simonis [69]. According to these numbers, copper smelters would produce 3.2–5 times lower Cd emissions than lead smelters. These emissions are primarily related to pyrometallurgical operations. Emissions in hydrometallurgical/electrolytic plants are likely to be negligible unless the sulfuric acid tanks are open to the atmosphere.

Approximately, 1 tonne of sulfur is associated with each tonne of primary copper in average ore. Emissions from primary copper smelters are principally particulate matter and oxides of sulfur ($SO_x$). Emissions are generated from the roasters, smelting furnaces, and converters. Fugitive emissions are generated during material handling operations. Copper and iron oxides are the primary constituents of the particulate matter, but other oxides such as arsenic, antimony, cadmium, lead, mercury and zinc, may also be present, along with metallic sulfates and sulfuric acid mist. Single stage electrostatic precipitators are widely used in the primary copper industry to control these particulate emissions. Because of considerable quantities of sulfur in the ores in which copper is found, significant emissions of sulfur dioxide occur from various processes associated with primary copper smelting. The

Table 8
Products, emissions, and energy use of copper smelters

| | Olympic Dam, Australia (1999–2003) | KUCC, USA (1998–2001) | Boliden's Rönnskär, Sweden (2001–2002) | Horne smelter, Canada (1997–2002) | Noranda/Falconbridge, Canada (2000–2003) | CCR, Canada (1997–2000) |
|---|---|---|---|---|---|---|
| Technology | Flash smelting-electric slag cleaning furnace | Flash smelting, double contact acid plant | Flash smelting | Bath smelting | Bath smelting | Electrolytic refining |
| Co-products | Au, Ag | Au, Ag, Mo, Se | Pb, Au, Ag, Zn | | | Au, Ag, Pt/Pd concentrate, Se, Te |
| Annual copper production (ktonne) | 160–200 (175) | 231–313 (285) | N/A | 147–196 (182) | 487–528 (504) | 235–340 (299) |
| $SO_2$ (kg/tonne Cu) | 15.0–19.1 (17.3) | 2.0–3.8 (2.7) | 14.1–15 (14.6) | 494–743 (580) | 110–170 (138) | 1.0–1.3 (1.2) |
| Energy (GJ/tonne Cu) | 19–25 (21) | N/A | N/A | 13.4–18.2 (16.2) | 20.6–22.8 (21.7) | 7–8 (8) |

Values in parentheses represent weighted average.

traditional roasters produce emissions with an average of 1–4% of $SO_2$ and 3–6% of the weight of the charged concentrate as particulate [70]. Primary copper smelters are a source of sulfur oxides ($SO_x$). The typical average $SO_2$ concentrations from various smelter units are summarized in Table 7.

#### 4.6.1. Flash smelting

A flash smelting process generates the highest concentrations of $SO_2$ (e.g., 15%) among those process routes, as the sulfide and fine coal instantly ignite and the oxidation of sulfur is very fast. Most of the sulfur dioxide is used to produce sulfuric acid plants. Usually, the sulfur dioxide fixation percentage can be as high as 99% or above for flash smelting process. With the adoption of flash smelting and flash converting at Kennecott Utah Copper Corporation (KUCC) in USA and the use of acid plant tail gas scrubbing at other plants (mainly in Japan) sulfur capture has exceeded 99.9%. The sulfur dioxide emission at KUCC's copper smelter is reportedly below 3.8 kg $SO_2$/tonne Cu [53].

By-product sulfur –mainly from copper smelters – is already a significant share of global elemental sulfur supply (around 19%) and will continue to be important for the next few decades. Sulfur can be fixed in metallurgical processes by either: sulfuric acid production, gas scrubbing and gypsum production, liquid sulfur dioxide manufacture, or elemental sulfur production. Sulfuric acid production is the most widely used process because it is the least expensive and the market for sulfuric acid is larger than for the other products in many locations.

The Sumitomo Toyo smelter in Japan uses the traditional Outokumpu flash smelting process and Peirce-Smith converters. It has distinct differences from other smelters around the world that use that same technology. According to Toyo, it is designed to be one of the cleanest smelters in the world. The sulfur fixation at Toyo is 99.9%, which is accomplished with fugitive gas collection, automated charging of converters and tail gas scrubbing. At the Toyo copper smelter, the sulfur distribution is as of $H_2SO_4$ 95.8%; gypsum 2.9%; slag 1.1%; water treatment 0.1%; emission 0.1% [51].

Modern smelters achieve high sulfur fixation through using flash smelting technology with the integrated acid plant of double contact adsorption technique. This has been well demonstrated by KUCC in USA. Before 1993, the total $SO_2$ emission from KUCC's smelter was as high as ~110 kg $SO_2$/tonne Cu (By 1990, Kennecott's acid plants recovered about 93% of the sulfur.) The new KUCC's smelter, started in 1995, is designed to recover 99.9% of the sulfur produced [71]. The copper concentrate is smelted in an Outokumpu flash smelting furnace. Matte is granulated and processed using a Kennecott–Outokumpu flash converting furnace. To achieve a sulfur capture in excess of 99.9%, the design incorporates the following: Continuous processes for the production of copper matte and blister copper, elimination of ladle transfers of molten metal, secondary gas collection at tapping and other furnace locations, secondary gas scrubbing, concentrate dryer off-gas scrubbing, anode furnace off-gas scrubbing and an acid plant designed to treat a feed of 14% sulfur dioxide down to less than 100 ppm sulfur dioxide [53]. A sulfur capture of 99.9% is equal to 2 kg $SO_2$/tonne copper produced. It is one of cleanest copper smelters in the world.

At KUCC, molybdenum is recovered as a by-product of the copper processing operations at its copper concentrator. Normally, approximately 8180 tonnes of molybdenum are recovered each year through the flotation process.

The Olympic Dam smelter in Australia also uses flash smelting technology [72]. The emission factors for $SO_2$ of these two smelters are listed in Table 8. In 2003, the Olympic Dam smelter achieved sulfur dioxide fixation of 99.4%, which gave an emission level of 15 kg $SO_2$/tonne Cu. As shown in this table, the emissions of $SO_2$ generated from KUCC's modernized flash smelting furnace are lower than those from the Olympic Dam smelters.

At KUCC, in 2003, total $SO_2$ emissions from the smelter were 966.8 tonnes, which means that 965,833 tonnes of $SO_2$ were captured by the pollution control equipment—the double contact acid plant. Of the total $SO_2$ emissions from KUCC's operations, the smelter represented approximately 27%, while the remaining sulfur dioxide emissions from operations largely result from fuel usage in the power plant (71%), while $SO_2$ emissions from the mine mobile equipment were minimal (0.01%) [73].

The KUCC's low $SO_2$ emission is accomplished by: continuous processes for the production of copper matte and blister copper, elimination of ladle transfers of molten metal,

Table 9
Electricity consumption for copper process stages [79,80]

| | 3% Cu ore[a] | 1% Cu ore[b] |
|---|---|---|
| Electro-refining route (kWh/tonne) | | |
| Mining | 433 | |
| Milling | 1233 | |
| Subtotal | 1666 | 3556 |
| Smelting | 430 | |
| Refining | 300 | |
| Subtotal | 730 | 4178 |
| Total | 2396 | 7733 |
| | | 2% Cu ore[a] |
| Hydrometallurgical route (kWh/tonne) | | |
| Mining | | 650 |
| Crushing | | 100 |
| Subtotal | | 750 |
| Leach/SX | | 2500 |
| EW | | 2000 |
| Subtotal | | 4500 |
| Total | | 5250 |

[a] *Source*: [80].
[b] *Source*: [79].

secondary gas collection at tapping and other furnace locations, secondary gas scrubbing, concentrate dryer off-gas scrubbing, anode furnace off-gas scrubbing and double contact acid plant [53].

In Europe, Boliden's Rönnskär smelter in northern Sweden extracts base metals and by-products from concentrates and recycled raw materials [74]. Rönnskär is one of the world's largest facilities for the recycling of base metals from electronic scrap as well as other secondary raw materials. The major products of Rönnskär are copper, lead, gold, silver and zinc clinker. It also produces crude selenium (95% selenium) as well as copper telluride (33% copper, 35% tellurium, and 6% silver) in the process at the precious metals plant. The portion of total metal production derived from recycling was 20% for copper, 40% for gold, and 90% for zinc. Copper concentrate is processed using flash smelting technology. The sulfur at Rönnskär is recovered as sulfuric acid and liquid sulfur dioxide. It is reported that the fixation of sulfur dioxide exceeded 99%. In the precious metals plant, Kaldo furnace is used to process and recover selenium.

The emissions quantities for 2001 and 2002 of this smelter are listed in Table 8. It was calculated that the emission of $SO_2$ of 2002 was 18.5 kg $SO_2$/tonne Cu, which is in the same level as the emissions of the Olympic Dam smelter in Australia.

Summarily, in flash smelting operations, sulfur dioxide fixation percentage can be as high as 99% and even better.

### 4.6.2. *Mitsubishi smelting process*

This process is used in Falconbridge Limited, Kidd Metallurgical Division. Its copper smelter consists of three furnaces (smelting, slag cleaning, and converting), interconnected by gravity flow launders. Electrostatic precipitators and scrubbers are used in this plant. The acid plant is a double contact, double adsorption plant with a design conversion efficiency of 99.5%. The gas effluents contain about 10% of sulfur dioxide, a large fraction of which is recovered as liquid sulfur dioxide. As shown in Table 4, the sulfur dioxide emission is controlled below 20 kg $SO_2$/tonne metal in this plant.

### 4.6.3. *Bath smelting*

Traditional copper smelters usually have much higher emission of sulfur dioxide due to the difficulty of recovering sulfur dioxide associated with the use of reverberatory furnaces. Consequently, without acid plants to treat sulfur dioxide, the emission factor of $SO_2$ can be as high as 1000 kg $SO_2$/tonne Cu. Noranda's Horne smelter utilizes bath smelting technology. It processes copper concentrates, copper and precious metal-bearing recyclable materials and other complex, high-margin material. This smelter produces copper anodes of 99.1% Cu. The smelter (bath smelting process) had $SO_2$ emission levels of 552,000 tonnes in 1980 and 420,000 tonnes in 1988 before a sulfuric acid plant in services in 1989. The emission levels of $SO_2$ at Horne smelter are listed in Table 8.

As seen from the above table, the $SO_2$ emission is much higher compared to flash smelting. The Noranda's facilities in Canada are one of the world's largest producers of zinc, nickel and copper. The copper is produced using a bath smelting technology. The average emission factors from Noranda's smelters in Canada are listed in Table 8.

Apparently, as can be seen from Table 8, the $SO_2$ emission from a bath smelter is much higher than that of from flash smelting smelter. 82.6% of sulfur fixation was achieved in 2003 in Noranda's smelters. Its target is for its Canadian operations to achieve 90% capture of sulfur, a 57% reduction from the 1985 release level. Compared to 99% sulfur dioxide fixation of flash smelting, the bath smelting has only around 90% of sulfur dioxide fixation.

Table 10
Energy consumption for different types of smelting technologies, GJ/tonne metal refined

| Smelters | Technologies | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 |
|---|---|---|---|---|---|---|---|---|
| Olympic Dam | Flash smelting, Cu | 25.7 | 30.7 | 25.1 | 19.4 | 19.5 | 20.6 | 21.8 |
| Kidd Creek | Mitsubishi continuous, Cu, Zn | 26.4 | 23.8 | 24.2 | 24.2 | 24.9 | N/A | N/A |
| Horne & CCR | Bath smelting, Cu | 23.0 | 21.5 | 25.4 | 26.0 | 23.3 | 23.8 | N/A |
| Rönnskär smelter[a] | Flash smelting, Cu, Pb, Zn | N/A | N/A | N/A | 20.8 | 14.2 | 14.3 | N/A |

[a] 20% of copper, 90% of zinc productions from recycled materials, respectively.

Table 11
Life cycle inventory of energy and emissions for mining and smelting of Cu and co-products

| | Allocation criteria | | | |
|---|---|---|---|---|
| | Mass[a] | Economic value[b] | | |
| | Cu/Mo/Se/Te | Cu | Mo | Se |
| Energy (GJ/tonne) | | | | |
| Mining[c] | | | | |
| Electricity | 1.3 | 0.9 | 3.8 | 5.0 |
| Fuel oil | 1.2 | 0.8 | 3.5 | 4.6 |
| Smelting/refining[d] | | | | |
| Electricity | 7.6 | 5.2 | 22.2 | 29.3 |
| Coal | 3.8 | 2.6 | 11.1 | 14.7 |
| Natural gas | 10.0 | 6.8 | 29.4 | 38.8 |
| Fuel oil | 1.6 | 1.1 | 4.6 | 6.0 |
| Emissions to air (g/tonne) | | | | |
| Mining | | | | |
| Particulate | 60 | 41 | 176 | 232 |
| Smelting/refining[e] | | | | |
| $SO_2$ | 2200 | 1500 | 6500 | 8600 |
| Ag | 0.8 | 0.5 | 2.7 | 3.1 |
| As | 2.8 | 1.9 | 10.0 | 11.4 |
| Cd | 0.4 | 0.3 | 1.4 | 1.6 |
| Cr | 0.8 | 0.5 | 2.7 | 3.1 |
| Cu | 81.8 | 55.3 | 293 | 334 |
| Hg | 0.015 | 0.010 | 0.054 | 0.062 |
| Mn | 0.4 | 0.3 | 1.4 | 1.6 |
| Ni | 0.76 | 0.51 | 2.7 | 3.1 |
| Pb | 13.2 | 8.9 | 47.2 | 53.7 |
| Sb | 0.8 | 0.5 | 2.7 | 3.1 |
| Se | 0.8 | 0.5 | 2.7 | 3.1 |
| Ta | 0.4 | 0.26 | 1.4 | 1.6 |
| V | 0.4 | 0.3 | 1.4 | 1.6 |
| Zn | 1.5 | 1.0 | 5.4 | 6.2 |
| Emissions to water (g/tonne) | | | | |
| Mining | N/A | N/A | N/A | N/A |
| Smelting/refining[e] | | | | |
| Ag | 0.4 | 0.3 | 1.4 | 1.5 |
| As | 1.1 | 0.77 | 4.1 | 4.6 |
| Cd | 0.4 | 0.26 | 1.4 | 1.5 |
| Cr | 0.4 | 0.26 | 1.4 | 1.5 |
| Cu | 1.1 | 0.77 | 4.1 | 4.6 |
| Hg | 0.006 | 0.004 | 0.022 | 0.025 |
| Mn | 0.4 | 0.3 | 1.4 | 1.5 |
| Ni | 1.1 | 0.77 | 4.1 | 4.6 |
| Pb | 0.2 | 0.13 | 0.7 | 0.8 |
| Sb | 0.4 | 0.3 | 1.4 | 1.5 |
| Se | 1.8 | 1.2 | 6.5 | 7.4 |
| Ta | 0.4 | 0.3 | 1.4 | 1.5 |
| V | 0.4 | 0.3 | 1.4 | 1.5 |
| Zn | 1.1 | 0.77 | 4.1 | 4.6 |

[a] [67].
[b] [56,81,82].
[c] Three percent of ore concentration, mostly open-pit mining, source [38].
[d] Estimated from Table 10 and [39].
[e] [46].

### 4.6.4. Emissions from electrolytic refining of copper

To produce copper cathode, an electrolytic refining process is involved. The electrolytic refining does not produce emissions to atmosphere unless the associated sulfuric acid tanks are open to the atmosphere. However, spent electrolyte and wash water contain significant amount of metal compounds in solution and usually need to be treated prior to discharge. The Canadian copper refinery (CCR) of Noranda processes copper anodes from the Horne and Altonorte smelters as well as secondary feed from other third party sources. Along with the production of copper cathode, the CCR produces gold, silver, platinum/palladium concentrate, selenium, and tellurium. In 2003, this refinery produced 235,000 tonnes of copper cathode, approximately 1.1 million ounces of gold, 30.3 million ounces of silver and other by-products. As a typical electrolytic copper refinery, its energy consumption and emission levels are listed in Table 8. Despite increasingly effective sulfur recovery, not all the sulfur is recovered from the ore itself, and even more remains with the gangue and overburden.

A primary copper processing primarily generates two solid-phase wastes; slag and blowdown slurry/sludge. Slag is generated during the smelting, converting, fire refining, and electrolytic refining stages. Slag from smelting furnaces is higher in copper content than the original ores taken from the mines. These slags therefore, may be sent to a concentrator and the concentrate returned to the smelter. This slag processing operation results in slag tailings. Slag resulting from converting and fire refining also is normally returned to the process to capture any remaining mineral values. Blowdown slurry/sludge that results from the sulfur recovery process is regulated as hazardous waste [75].

## 4.7. Energy factors in the co-production of Cu, Mo, Se, and Te

Energy is a major element in the cost of copper production. Typically, the specific energy consumption (SEC) of primary copper production is in the range of 25–30 GJ/tonne of refined copper for pyrometallurgical process. In general, the SEC of hydrometallurgical technologies is higher than that of pyrometallurgical processes [76,77]. The breakdown of the SEC by process operations is approximately as follows: open-pit mining, 20%; concentration, 50%; smelting, 17%; refining, 13%.

The reported energy consumption as of 1992 from the production of 1 metric tonne of copper from concentrate and scrap in Germany was 21.8 GJ, which was split as: 6.3 GJ for the production only and 15.5 GJ attributed to the electricity and other. The same author also reported that the energy consumption for the production of 1 metric tonne of copper from secondary materials was split as: 9.21 GJ for the production only, and 11.34 GJ for the electricity and other [78].

It is obvious that the electricity requirements for the production of copper is quite sensitive to the original copper ore grade. For example, to produce 1 tonne of refined copper with ore grade of 3.0% Cu, the electricity consumption is assumed to be around 2396 kWh/tonne Cu (8.6 GJ equiv./tonne), whereas it may need 7733 kWh/tonne Cu (27.8 GJ equiv./tonne) of electricity to produce 1 tonne of refined copper from ore grade of 1.0% Cu (Table 9).

As shown in Table 10, the typical energy consumption in primary copper production is fall in the range of 20–25 GJ/tonne, among which, 13–16 GJ/tonne of energy is used in firing smelting unit and 6–8 GJ/tonne of energy is consumed in the electrolytic refining process. Table 11 presents the life cycle inventory (LCI) for the mining and smelting stages of Cu and co-products. The energy data for the mining stage describes the US average condition in 1997, when 28 of 38 operating copper mines were open-pit type [38]; open pit requires much lower energy than underground mining. For the smelting and refining stages, the energy estimate corresponds to an industry average while emissions data represent the KUCC's condition [73].

## 5. Current trends and future outlook

The most profound trends in the production of metals over the last 10 years has been the adoption of new, environmentally friendlier technologies, use of the sulfur content of the ores and adding pollution control equipment. Adopting new technologies is likely going to continue as old facilities are phased out and new ones are added. Much of the recent technological research and development has focused on improving leaching and metallurgical processes. In primary zinc production, hydrometallurgical separations have substituted smelting in most North American facilities. The shift to electrolytic processing drastically reduced cadmium emissions because it eliminated the sintering step in zinc refining, and thus, much of the particulates burden. Also, the early practice of roasting zinc sulfide and discharging the $SO_2$ into the atmosphere was replaced by converting the gas to sulfuric acid.

The same is expected to happen in copper production. The need for refined copper is likely to increase as China and India are increasing their consumption. Implementation of the SX–EW process is gaining momentum, and this has economic advantages as it allows for the economic processing of low-grade material. Industry representatives predict that the industry is only a few years away from widespread hydrometallurgical treatment of copper–iron sulfide ores [83] (likely through bacteriological leaching [84]) and copper concentrates (through reacting in a high temperature pressure vessel). In both cases, refined copper could be produced without the need for smelting and refining.

On the other hand, the energy factors in the mining industry have been increasing moderately, because less concentrated ores are being processed, and because electrolytic production although it generates much lower direct emissions, it uses more energy than the pyrometallurgical processes it replaces.

In this article, we only covered primary metal production starting from the mining of the metal-carrying ores. However, for the base metals, especially aluminum and copper, there is a substantial secondary production through recycling of used products. Secondary metal production generates much lower emissions and requires less energy than primary production. Copper from ore requires five to seven times more energy than that required for processing recycled metal and this ratio rises with decreasing ore grade. Aluminum from ore uses approximately 20 times more energy than from recycled metal [71,84].

## 6. Discussion/conclusion

The life cycle inventory data of minor metals studied in this paper are fundamental building blocs for compiling the full life cycle effect of PV modules. However, the databases commonly used in life cycle analysis (LCA) are lacking data for most minor metals used in the production of photovoltaics. In addition, data for major metals, i.e., zinc, lead, and copper, need to be updated as presented in this paper, as industries are striving for more sustainable production technologies, concurrently producing the minor metals in more benign ways. Data deficiency or inaccurate presentation of such data may cause incomplete analyses or large uncertainties in the final results. We reviewed, in this paper, the most up-to-date energy and emissions data of mining, smelting, and refining the minor metals whose life cycle inventories were unavailable or needed an update.

Cadmium, indium, germanium, gallium, selenium, and tellurium are mined and produced as by-products of major metals. These metals will be disposed as waste, if not processed. We allocated emissions and energy usage to these metals on the basis of mass and economic values. Avoiding allocation, which most fairly delineates the effect of producing minor metals, was impossible owing to the integrated data reporting with major metal processes. In a previous study [13], we showed that for Cd, avoiding allocation results in lower emissions than allocating based on mass or economic values. The same will be true for the life cycle inventory figures estimated in this paper.

This article describes the extraction of metals from primary sources, but aluminum, copper, indium, gallium, and selenium are also recovered from recycled material. This could be an area for further studies.

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